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PROCESS MODIFICATIONS TOWARDS MINIMIZATION OF ENVIRONMENTAL POLLUTANTS IN THE CHEMICAL PROCESSING INDUSTRY

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The report covers the development of a matrix of significant pollution problems and attendant process modifications which would have impact on the reduction or elimination of pollutants inherent in these processes. Industries covered are: (1) Refining of Nonferrous Metals; (2) The Electroplating Industry; (3) Coal Conversion Processes; (4) Specialty Chemicals; (5) The Paper & Pulp Industry; (6) Iron and Steel Industry; (7) The Primary Aluminum Industry; and (8) Phosphate Fertilizer Industry.

The matrix for each of the industries noted covers the individual process; the pollutants and their sources in the process; the nature of the pollutant and the control strategy for mitigation or reduction of the pollutant.

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LIST OF ABBREVIATIONS

Abbreviation	Terms
cfm	cubic feet per minute
ft^3	cubic feet
g/l	grams per liter
K.W.H.	kilowatt hours
m^3	cubic meters
mm	milimeters
MG	million gallons
N-K-P	nitrogen, potassium, phosphorous ratio
ppm	parts per million
scf	standard cubic feet
SNG	synthesized natural gas
µm	microns

INTRODUCTION

The objective of this planning project on Process Modification Towards Minimization of Environmental Pollutants in the chemical process industry is to suggest fundamental research studies which will have significant impact in the minimization of industrial pollutants. Towards this end, eight industries are surveyed to develop a matrix of significant pollution problems and attendant process modifications which would have impact on the reduction or elimination of pollutants inherent in these processes. The industries surveyed are as follows:

1. Refining of Nonferrous Metals
2. The Electroplating Industry
3. Coal Conversion Processes
4. Specialty Chemicals
5. The Iron and Steel Industry
6. The Paper and Pulp Industry
7. The Primary Aluminum Industry
8. Phosphate Fertilizer Industry

Although these industries are diverse, it is apparent that generic pollution problems cut across most of these and other industries not covered in the survey. Accordingly, various process modification strategies and attendant research programs which would minimize these pollution problems and are generic in nature, are indentified.

CHAPTER 1

REFINING OF NONFERROUS METALS

1.1 INTRODUCTION

This chapter will concentrate on the refining of nonferrous metals from mineral ore. The sections of this chapter are divided as follows:

1. Copper Production by Pyrometallurgical Processes
2. Copper Production by Hydrometallurgical Processes
3. Uranium Production by Hydrometallurgical Processes.

1.2 COPPER PRODUCTION BY PYROMETALLURGICAL PROCESSES

Ninety percent of the world's primary copper originates in the sulphide form. A vast majority of this copper is extracted by pyrometallurgical techniques because sulphide ores are not easily leached. Typical copper deposits contain only 1 to 2% copper, therefore, the ore must undergo several process steps to concentrate the copper before smelting. This method of copper extraction includes the following steps (Biswas and Davenport, 1980):

1. Concentration by Froth Flotation
2. Roasting
3. Matte Smelting
4. Converting to blister copper
5. Electrorefining

The pollutants of primary concern include SO_2, particulates, slag, and dissolved metal salts in various effluent streams (Barbour, 1980). Figure 1.1 is a flow chart of this process, indicating the numerous ways in which copper concentrate can be smelted to produce blister copper.

Other sources of waste water include acid plant blowdown, slag granulation, and cooling of the hot metal anodes. Electrorefining also generates waste through spent electrolyte, washing cathodes, and the recovery of slime (U.S. EPA, Feb. 1975).

1.2.1 Comminution and Froth Flotation

A copper concentrate is produced by a series of flotation cells which selectively float copper sulphide to the surface of the bath so the concentrate can be skimmed off the top. This process is depicted in Figure 1.2. The tailings taken from the tank are piped to evaporation ponds where the water is clarified and recycled (Biswas and Davenport, 1980).

The tailings require pH adjustments and extraction of arsenic, cyanide, and some metals. The amount of water consumed for this process step can be reduced if improvements are made to the grinding efficiency of the dry ore.

1.2.2 Roasting of Copper Concentrate

The copper concentrate can be refined by several different methods of roasting and/or smelting as shown in Figure 1.1. Roasting of sulphide concentrates produce calcines for leaching or for reverbatory (or electric) furnace smelting. The

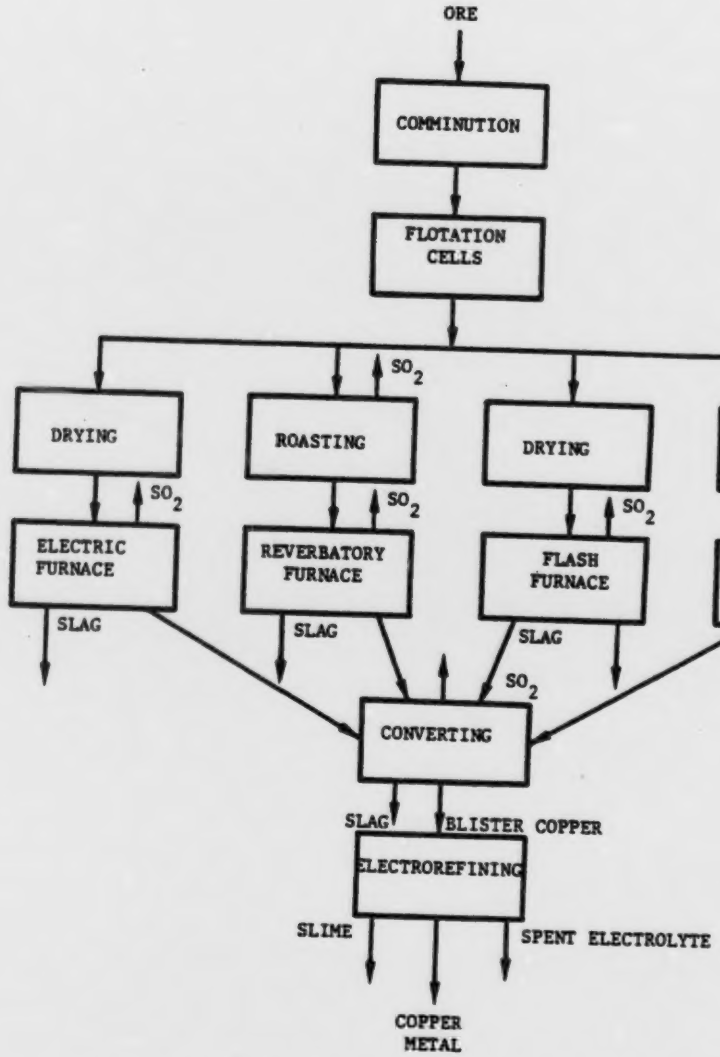
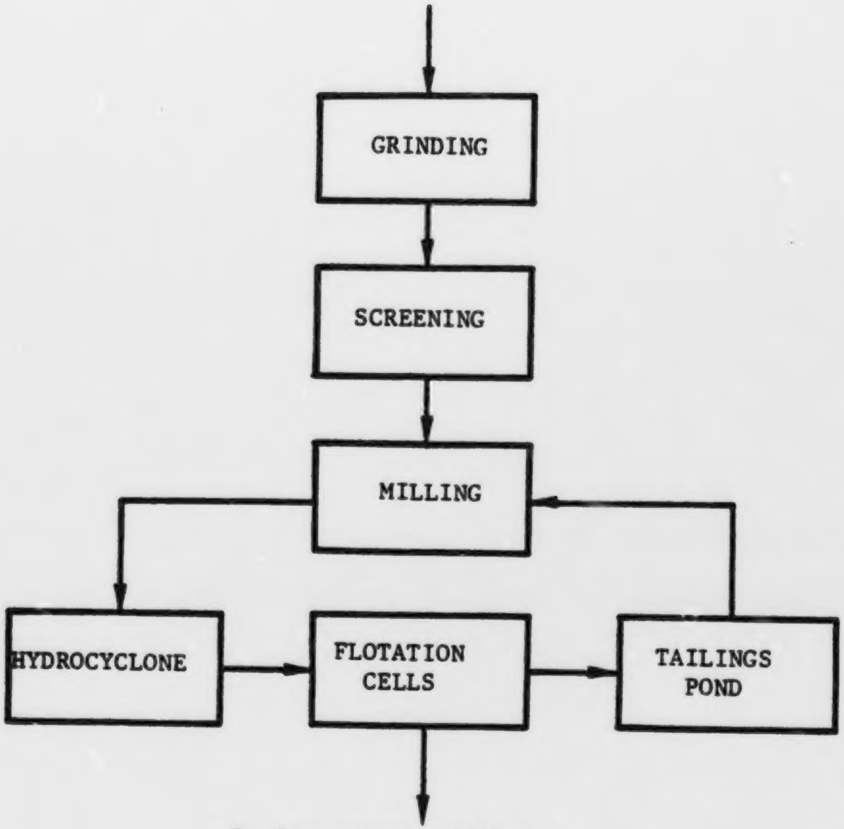

ORE
COMMINUTION
FLOTATION CELLS
DRYING
ROASTING
DRYING
SINTERING
SO_2
ELECTRIC FURNACE
REVERBATORY FURNACE
FLASH FURNACE
BLAST FURNACE
SLAG
CONVERTING
BLISTER COPPER
ELECTROREFINING
SLIME
SPENT ELECTROLYTE
COPPER METAL

Figure 1.1. Flow Chart Showing the Principal Process Steps For Extracting Copper from Sulphide Ores. (Biswas and Davenport, 1980).


GRINDING
SCREENING
MILLING
HYDROCYCLONE
FLOTATION CELLS
TAILINGS POND

Cu Concentrate (24% Cu)

Figure 1.2. Comminution and Froth Flotation (Biswas and Davenport, 1980).

fluid-bed roaster is the best device for sulphide roasting since it has a high production rate and produces 5-15% by volume SO_2 in the flue gases which can be easily converted into usable forms of sulfur (Gill, 1980).

1.2.3 Smelting

The process of smelting and converting vary widely in equipment design but the pollutants are essentially the same: SO_2, particulates, and slag. There are several reasons for cleaning gases from metallurgical processing, the most important of these are (Gill, 1980):

1. To recover value-bearing particulate material which can be returned to the plant for reprocessing.
2. Environmental pollution, from the viewpoint of employees exposed to harmful gases and, SO_2 combining with atmospheric water vapor to form acid rain, damaging plants and injuring animals.
3. To remove value-bearing gaseous by-products such as SO_2, which can be used as the feed material for the production of marketable sulfuric acid or elemental sulfur.
4. To recover fuel value of gaseous by-products like combustible CO.
5. To reclaim the sensible heat to the flue gases in waste heat boilers.

Optimization of the smelter design can reduce the amount of environmental pollution or alter the effluent streams so that the pollutants can be easily removed. If the SO_2 concentration is greater than 4% by volume, it can be converted into sulphuric acid without much difficulty. Typically SO_2 is converted into sulphuric acid, sulfur, or ammonium sulfate.

A survey of metals in various process streams was taken at a smelting plant owned by the Radian Corporation in Austin, Texas. Table 1.1 is a compilation of the flow rates (Schwitzebel, et al. 1978). Some of the streams were not measured or recorded but the chart does illustrate the number of different elements present in the effluent streams.

TABLE 1.1. FLOW RATES OF METALS IN PROCESS STREAMS

	Flow Rate lb/hr				
Element	Feed	Matte	Slag	Flue Outlet	ESP Catch
Al	400	17	700	0.10	1.1
As	190	48	48	76	30
Ba	31	33	43	0.64	0.023
Be	0.072	4.1×10^{-3}	0.032	0.0034	0.0004
Ca	770	12	1900	0.011	2.1
Cd	59	37	0.33	0.076	0.74
Cr	0.076	0.64	3.8	0.044	0.018
Cu	16000	18000	220	1.8	62
F	3.4	0.012	2.2	9.4	0.032
Fe	10000	11000	12000	0.55	42.6
Hg	0.018	0.020	0.0091	0.033	0.00015
Mo	79	8.5	89	0.17	6.6
Ni	0.70	2.0	0.76	0.011	0.059
Pb	49	84	13	0.38	5.3
Sb	6.0	4.6	3.4	0.030	1.3
Se	10	0.17	5.5	0.65	0.16
Si	1100	42	4800	1.7	1.7
V	0.92	0.33	0.86	0.027	0.011
Zn	42	31	30	0.22	4.6

To recover the metals from the captured particulates, it may be possible to use acid leaching and solvent extraction to selectively remove metals from low concentration leach solutions.

1.2.4 Electrorefining

Electrorefining is the final step of purifying blister copper to 99.99% Cu which can be used for most industrial applications. The spent electrolyte is recycled, but some of the acid must be treated to remove excess nickel and unclaimed copper as well as other trace metals. Slime develops from the particulates and precipitates and must be treated to recover copper and/or precious metals. Figure 1.3 is a flow chart illustrating the representative steps of the electrorefining process (U.S. EPA, Feb. 1975).

Table 1.2 lists the concentration ranges of several priority pollutants contained in the designated process streams. Slime is either discarded or undergoes further treatment for recovery of trace metals. A bleed from the electrolyte, water used to wash the anodes during preparation, and slime are the primary sources of water contamination from the electrorefining process.

Table 1.3 summarizes the pollutants and suggested control strategy for copper production by pyrometallurgical processes.

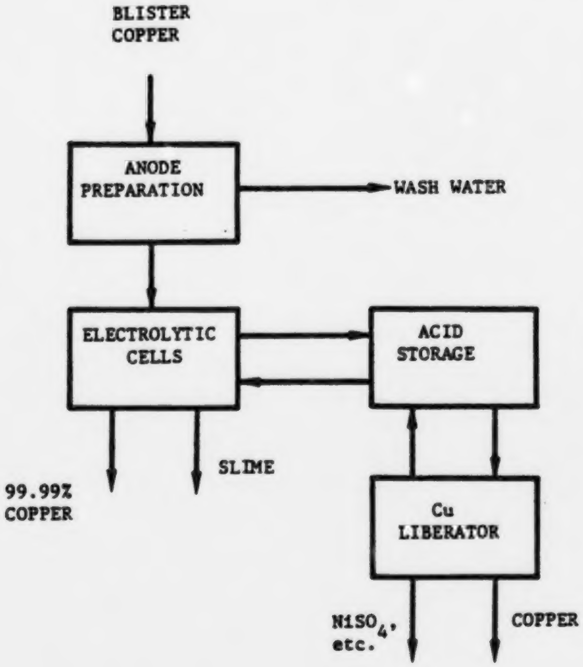

BLISTER COPPER
ANODE PREPARATION
WASH WATER
ELECTROLYTIC CELLS
ACID STORAGE
99.99% COPPER
SLIME
Cu LIBERATOR
$NiSO_4$, etc.
COPPER

Figure 1.3. Flow Chart for Electrorefining Process (U.S. EPA, Feb. 1975).

Table 1.2. Concentration Ranges in Effluent Streams from Electrorefining Process (U.S. EPA, Feb. 1975)

POLLUTANT	ELECTROLYTE (g/L)	SLIME (%)
Antimony	0.2 to 0.7	0.5 to 5.0
Arsenic	0.5 to 12.0	0.5 to 4.0
Copper	45.0 to 50.0	20.0 to 40.0
Lead		2.0 to 15.0
Nickel	2.0 to 20.0	0.1 to 2.0
Selenium		1.0 to 20.0
Silver		3.4 to 27.4

Table 1.3 summarizes the pollutants and suggested control strategy for copper production by pyrometallurgical processes.

1.2.5 Recommended Areas for Process Modifications Research

After evaluating the available literature, the following areas are recommended for further research by the study:

- Optimization of the communition of dry mineral ore to reduce the amount of water used in froth flotation.
- Recover value-bearing products by dissolving the metals from particulates collected in the electrostatic precipitators and use solvent extraction procedures to extract the desired products.
- Use solvent extraction to recover copper or other metals from effluent streams before the water is sent to the tailing ponds.
- Improve smelter design to contain and eliminate the release of SO_2 and other hazardous flue gases into the atmosphere.

Table 1.3. Pollutants and Suggested Control Strategy for Copper Production by Pyrometallurgical Processes

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Ore grinding	Particulates	Crushers grinders, ball mill etc.	Inorganic	Electrostatic precipitator
Froth flotation	Metals, Dissolved sludge, cyanide, pH etc.	Tailings	Inorganic and organic additives	Solvent extraction, evaporation, tailings pond
Smelting (a) Reverb (b) Electric (c) Flash (d) Blast	SO_2, slag and particulates	Flue gases, slag dump	Inorganic and Gaseous SO_2	Acid plant for SO_2, ESP, solvent extraction
Converting	SO_2 slag and particulates	Flue gases, slag dump	Inorganic and gaseous SO_2	Acid plant, ESP, solvent extraction
Anode preparation	Dissolved metals, H_2SO_4	Anode wash	Inorganic	Solvent Extraction
Electro-refining	Dissolved metal, H_2SO_4	Electrolyte, cathode cooling etc.	Inorganic	Solvent extraction

1.3 COPPER PRODUCTION BY HYDROMETALLURGICAL PROCESSES

Hydrometallurgy has three advantages over the smelting and converting processes that are traditionally used for the manufacture of copper. First, leaching is a more economical method of extraction when the ore has a low concentration of copper. Second, increasing energy costs of the furnaces is making pyrometallurgy less economical. Third, it is becoming increasingly difficult for smelters to meet stringent environmental regulations (Barbour, 1980).

The hydrometallurgical process entails three major steps; leaching, cementation (or solvent extraction), and electrowinning. This method of extracting copper from mineral ore has not been extensively applied to sulfide ores which are not readily leached. Due to the environmental problems associated with SO_2, hydrometallurgy is becoming a more acceptable method of producing copper (Biswas and Davenport, 1980).

1.3.1 Leaching

There are numerous methods of leaching and several types of leaching solutions. Sulfuric acid is commonly used as a leaching medium, but new technology has introduced other forms of leaching solutions such as ammoniacal and ferric chloride solutions. Leaching of sulfide ores can be improved by bacterial enhancement as well. The pregnant leach solution can undergo either solvent extraction, ion exchange or cementation to recover the copper while leaving the remaining trace metals in the leach solution (Wadsworth, 1980).

There are four methods of leaching (Wadsworth, 1979):

1. In situ leaching
2. Dump and heap leaching
3. Vat leaching
4. Agitated leaching

In situ and dump leaching are long term processes which can leach the ore with acid solution for several years. Due to this long period of exposure, significant quantities of the sulfide minerals will dissolve into the leach solution. Contamination of ground water may occur and could produce serious detrimental effects to the surrounding environment.

Vat leaching and agitated leaching are done with much smaller volumes of crushed ore at much shorter periods of exposure. These short term processes are useful for ores containing copper in the oxide form which dissolve easily in acid solutions. The pregnant leach solution is taken to refining process, while the remaining sludge is either dumped or recycled for additional processing to recover other metals that were not extracted.

If the leach solution has a high concentration of copper (40 to 60 g/1), it can be sent directly to the electrowinning circuit (Flett, 1974). When the solution has a low concentration, making direct electrowinning uneconomical, then a process step must be taken to separate the copper from the rest of the leach solution and redissolve the copper at a higher concentration into an electrolyte. Three commercially available processes that accomplish this task are cementation solvent extraction, and ion exchange.

1.3.1.1 Cementation

Cementation is a reaction where copper precipitates directly onto the surface of the scrap iron. The effluents contain very large quantities of iron salts and are generally sent to the tailings pond for waste treatment.

1.3.1.2 Solvent Extraction

Solvent extraction is a process having several circulation loops where copper ions are selectively extracted from a leach solution by a specific solvent. The extracted copper is stripped from the solvent which is then recirculated int the extraction circuit. The flow chart shown in Figure 1.4 illustrates the multiple circuits of the solvent extraction process.

Some of the pollution problems that exist in this process are the build up of trace metals in the leach solution and entrained solvent in the extraction and stripping sections. Problems associated with entrainment are complicated by the unavoidable degradation of the solvent. This reduces the extraction activity of the organic material and some make up must be added to the recycle.

Table 1.4 summarizes the pollutants and suggested control strategy for copper production by hydrometallurgical processes.

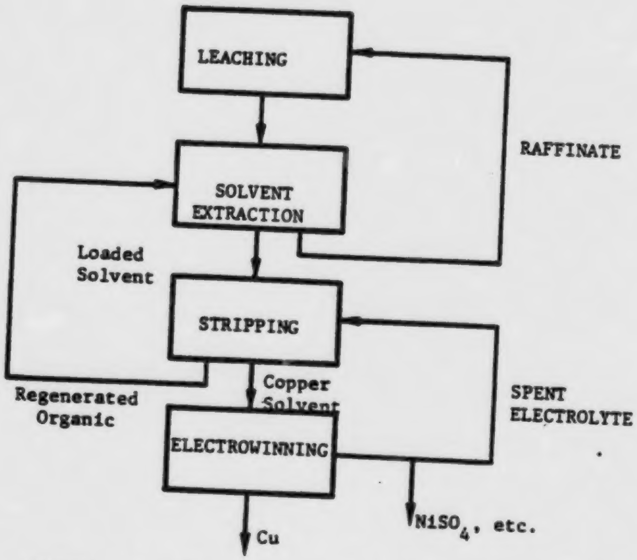

LEACHING
SOLVENT EXTRACTION
RAFFINATE
Loaded Solvent
STRIPPING
Regenerated Organic
Copper Solvent
SPENT ELECTROLYTE
ELECTROWINNING
Cu
NiSO4, etc.

Figure 1.4. Flow Chart of Solvent Extraction Process. (Gill, 1980).

Table 1.4 Pollutants and Suggested Control Strategy for Copper Production by Hydrometallurgical Processes

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Leaching in situ, heap, vat, agitated	Dissolved metal salts, sulfuric acid organic additives (wetting agents)	Leach solution	Inorganic, metals and acid	Recycle Leach solution after solvent extraction of excess metals, watch for seepage of metals into the ground water
Cementation	Dissolved metal salts	Iron ion from scrap iron	Inorganic	Solvent extraction of effluents
Solvent extraction	Dissolved metals, entrained solvents	Excess from process streams, solvent degradation	Inorganic metals and organic solvents	Improve mixer-settlers, study methods for regeneration of solvents
Electrowinning	Dissolved metals, acid, cyanide	Excess from process streams, cathode wash and cooling	Inorganic metals and acid	Solvent extraction of effluents

1.3.2 Recommended Areas of Process Modification Research

After evaluating the available literature, the following areas are recommended for further research by the study:

- Recover trace metals in the effluent streams by using solvent extraction. Conduct research in the area of simultaneous extraction of several metals that are considered hazardous pollutants.
- Recover entrained solvents by filtration, flotation, centrifugal separation, etc. Study the various methods of separating liquid-liquid mixtures and determine the best process to use.
- Solvents tend to degrade due to temperature, pH, or radiation extremes. Analyze the by-products of this degradation and determine the best way to eliminate these by-products either in the recycle stream or the exit stream.
- Evaluate new techniques for leaching sulphide ores or develop new techniques to improve selectivity in leaching mineral ores.

1.4 URANIUM PRODUCTION BY HYDROMETALLURGY PROCESSES

Uranium is becoming an important energy source since projected energy demands will greatly increase in the near future. Uranium content of a typical ore is in the order of 0.2 to 0.3 percent U_3O_8. For this reason, large quantities of material must be handled to mine and extract uranium. The conventional recovery processes include acid or alkaline leaching, solution purification, and product precipitation into yellow cake (U_3O_8). Solvent extraction and ion exchange have become the primary methods for solution purification and concentration of uranium values (Reed, et al. 1979). Figure 1.5 is a representation of a process flow chart for the refining of uranium ore.

1.4.1 Leaching

As mentioned in Section 1.3, there are numerous methods of leaching with varying degrees of ore preparation. Interest has increased in the use of in-situ leaching of underground deposits for uranium mining. The advantages of in-situ leaching are the significant reduction of processing costs and the minimal disturbance to the surface conditions. The subsurface deposit is flooded with leach solution and then pumped to the surface ready for uranium recovery. With in-situ leaching, the ore body remains intact and only the metal is removed, therefore a relatively small volume of waste requires disposal.

This method of leaching can only be done when the ore body is contained within a rock formation which is relatively impermeable, otherwise the ground water may become contaminated. The possibility of polluting fresh-water aquifers is present, particularly when a deposit is contained within an aquifer. Regulatory authorities require a "cleanup" of the deposit subsequent to the leaching operations. With proper design,

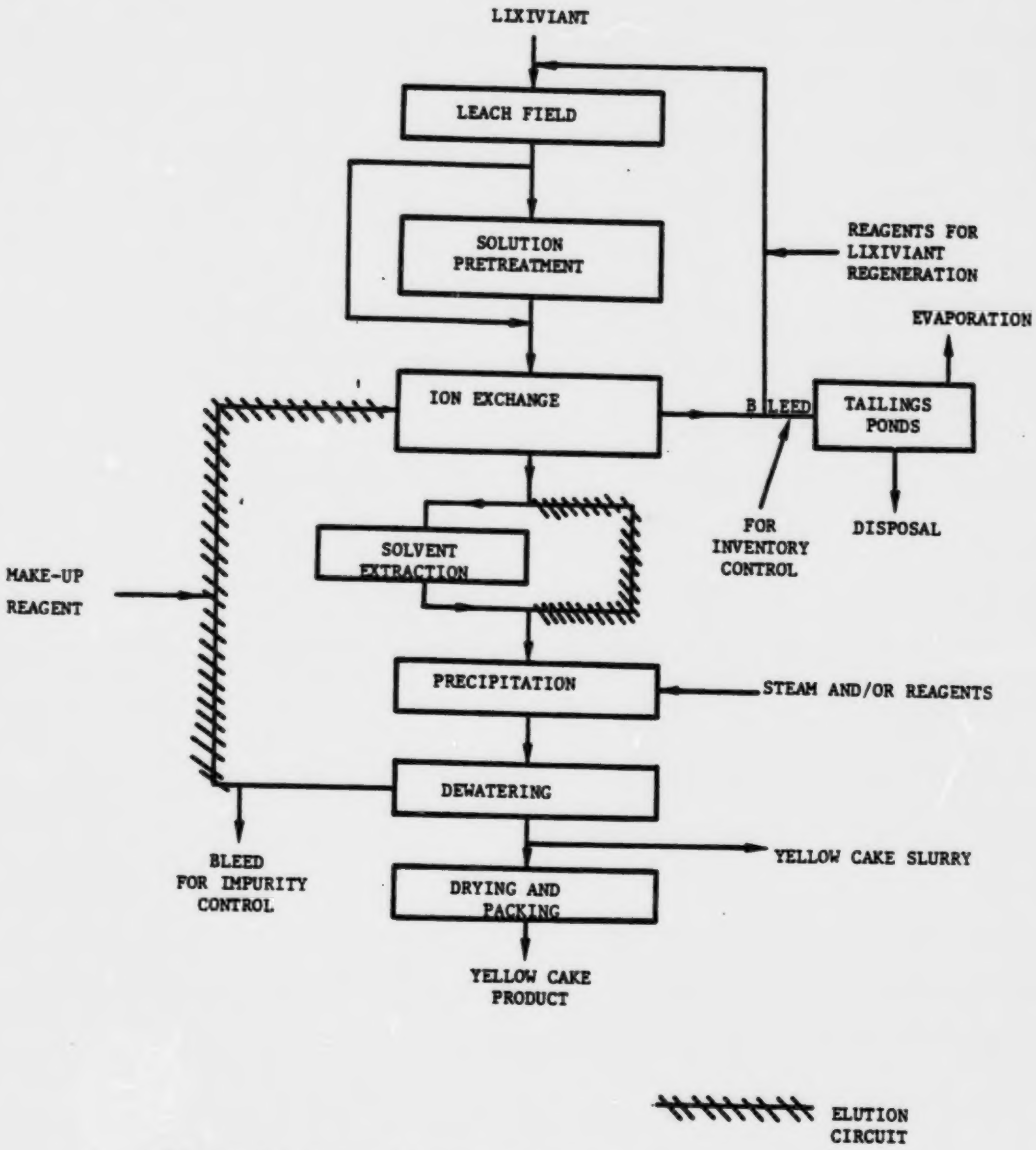

LIXIVIANT
LEACH FIELD
SOLUTION PRETREATMENT
REAGENTS FOR LIXIVIANT REGENERATION
EVAPORATION
ION EXCHANGE
BLEED
TAILINGS PONDS
FOR INVENTORY CONTROL
DISPOSAL
SOLVENT EXTRACTION
MAKE-UP REAGENT
PRECIPITATION
STEAM AND/OR REAGENTS
DEWATERING
YELLOW CAKE SLURRY
BLEED FOR IMPURITY CONTROL
DRYING AND PACKING
YELLOW CAKE PRODUCT
ELUTION CIRCUIT

Figure 1.5. Process Schematic for Uranium Recovery

operation, monitoring, and cleanup, in-situ leaching can be the most environmentally acceptable method of extracting metals from subsurface deposits.

Other methods of leaching can be used, but the damage to the surface, the amount of waste produced, and the costs for processing the ore will increase.

Uranium can also be recovered from leach solutions used for the extraction of other non-ferrous metals like copper, zinc, nickel, etc. Once the uranium is reclaimed from the leach solution it can be recycled into the leaching process after some "make-up" is added. A tailings pond is used to store the spent solution so that suspended particals are allowed to settle and the effluents can be contained without affecting the surrounding environment.

1.4.2. Solution Purification and Concentration

Leach solutions generally contain a large amount of impurities such as molybdenum, nanadium, selenium, iron, copper, etc. The concentration of pregnant solutions may range between .6 and 2.0 g/l U_3O_8. Solvent extraction techniques, and in some cases ion exchange are used to purify and concentrate the U_3O_8 in the solution. The final solution, after solvent extraction can be made to be 30 to 50 g/l. Ion exchange of clarified leach solution usually results in an elluant containing 10 to 12 g/l U_3O_8 (Reed, et al. 1979).

By using an ion exchange unit first and then a solvent extraction process, the amount of solvent required to recover the uranium may be greatly reduced. This modification has a tremendous economic advantage by reducing solvent inventory but may also lessen the pollution effects due to solvent entrainment and degradation.

1.4.3 Recommended Areas of Process Modification Research

After evaluating the available literature, the following areas are recommended for further research by the study:

- Evaluate new leaching solutions that may offer improvement in leaching selectivity and/or efficiency.
- Determine the best solvent for solvent extraction of uranium salts with minimal degradation.
- Divert recycle streams into additional process circuits to remove trace metals.

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CHAPTER 2

ELECTROPLATING

2.1 ELECTROPLATING OF COMMON METALS

Electroplating is a series of process steps that involves the preparation of the part in addition to the plating operation. Figure 2.1 is a flow chart of a chromium plating operation of zinc die castings. The sequence and/or the process steps may vary from plant to plant because of the many variables involved with electroplating. Table 2.1 is a list of pollutants that typically exist in the waste streams and their respective concentration ranges.

There are numerous methods of treatment for dissolved materials that exist in effluent streams. They are (U.S. EPA, April 1975):

- Ion Exchange
- Reverse Osmosis
- Electrodialysis
- Chemical Precipitation
- Ion Flotation
- Carbon Absorbtion
- Liquid-Liquid Extraction

Each method has advantages and disadvantages that must be considered with respect to the specific electroplating industry.

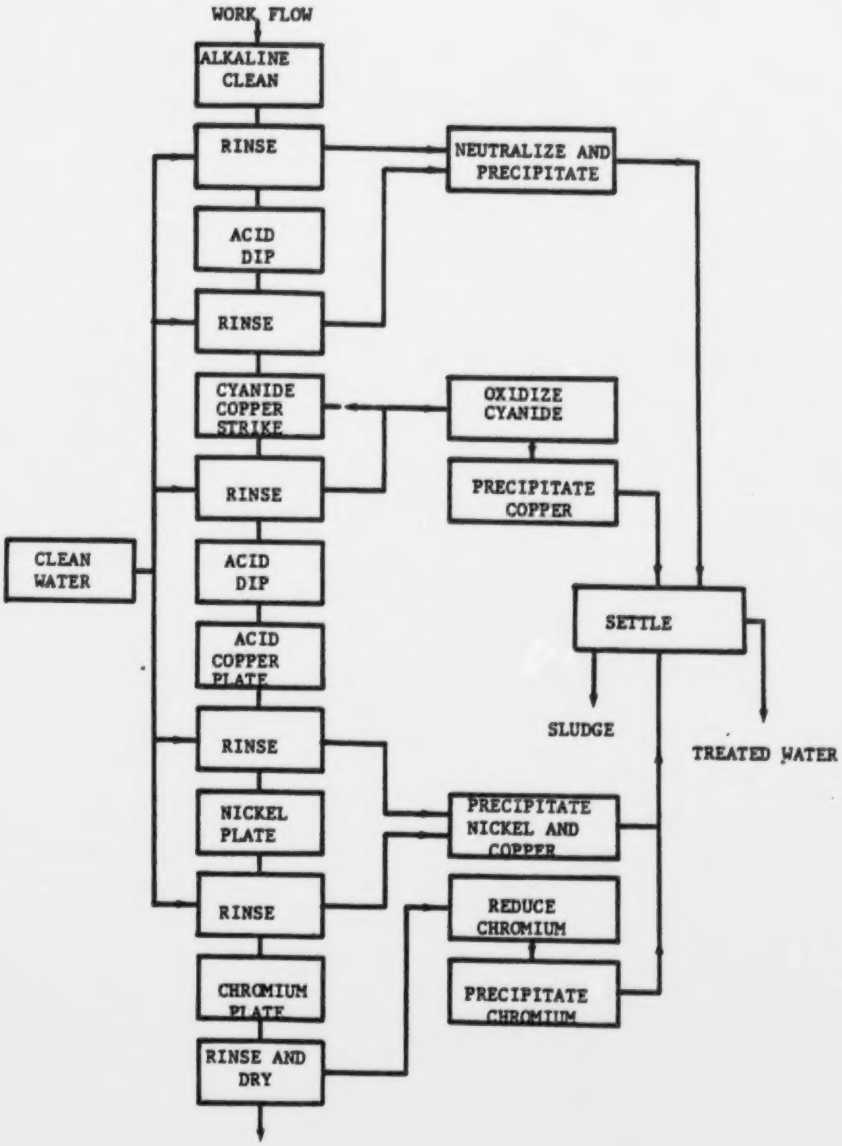
WORK FLOW
ALKALINE CLEAN
RINSE
ACID DIP
RINSE
CYANIDE COPPER STRIKE
RINSE
ACID DIP
ACID COPPER PLATE
RINSE
NICKEL PLATE
RINSE
CHROMIUM PLATE
RINSE AND DRY
CLEAN WATER
NEUTRALIZE AND PRECIPITATE
OXIDIZE CYANIDE
PRECIPITATE COPPER
SETTLE
SLUDGE
TREATED WATER
PRECIPITATE NICKEL AND COPPER
REDUCE CHROMIUM
PRECIPITATE CHROMIUM

Figure 2.1. Flow Chart for Water Flow in Chromium Plating Zinc Die Castings, Decorative (U.S. EPA, April 1975).

Since these recovery methods are readily available, similar methods can be adopted as additional process steps to remove trace metals before the water is recycled back into the process.

TABLE 2.1. COMPOSITION OF RAW WASTE STREAMS FROM COMMON METALS PLATING (U.S. EPA, August 1979)

	(mg/1)
Copper	0.032 - 272.5
Nickel	0.019 - 2954
Chromium, Total	0.088 - 525.9
Chromium, Hexavalent	0.005 - 334.5
Zinc	0.112 - 252.0
Cyanide, Total	0.005 - 150.0
Cyanide, Amenable to Chlorination	0.003 - 130.0
Fluoride	0.022 - 141.7
Cadmium	0.007 - 21.60
Lead	0.663 - 25.39
Iron	0.410 - 1482
Tin	0.060 - 103.4
Phosphorus	0.020 - 144.0
Total Suspended Solids	0.100 - 9970

2.1.1 Recommendations for Process Modifications

The best way to reduce the amount of water needed in an electroplating process is to maintain good "housekeeping" practices to avoid spillage or "dragout" of treating solutions into rinse waters. Other recommendations include:

- Substitute low concentration solutions in place of high concentration baths.
- Use non-cyanide solutions in place of the cyanide treatments.
- Use counter-flow rinses.
- Add a wetting agent to rinse waters.
- Install air or ultransonic agitation.
- Recover and reuse metals that are in effluent streams by solvent extraction.
- Recycle used rinse waters into the make-up solutions of their respective treating baths.

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CHAPTER 3

COAL CONVERSION PROCESSES

3.1 INTRODUCTION

The unpredictability of the international energy market and the very danger of global oil shortages in the next few decades have necessitated a rapid expansion in the domestic energy base in the U.S. Consequently, the commercial production of synthetic fuels from the abundant reserves of coal is a major objective of the nation's energy research and development programs. Coal liquefaction and coal gasification technologies have received renewed interest in this regard. Economic viability and environmental impact will be the limiting factors in the commercialization of such processes.

3.2 LIQUEFACTION

All coal liquefaction processes produce liquids from coal by yielding a material having a higher hydrogen content than coal. Fuel oils contain about 9% hydrogen and 14% gasoline as compared to roughly 5% hydrogen in raw coal. Currently, some twenty-odd liquefaction processes are in various stages of development by industry and federal agencies. Coal liquefaction technologies can be catagorized under hydrogenation, pyrolysis and hydrocarbonization, and catalytic synthesis. Of these, Hydrogenation is the most advanced (Koradek and Patel, 1978).

In this chapter, the environmental problems associated with the following four coal liquefaction technologies will be discussed:

1. Solvent Refined Coal, (SRC)
2. Synthoil
3. H-Coal
4. Exxon Donor Solvent

The following section will discuss the pollutant streams from and suggested control methods for the SRC process.

3.2.1 Solvent Refined Coal Liquefaction

A fully integrated SRC liquefaction system flow scheme (Shield, et al. 1979) is shown in Figure 3.1. Raw coal from the coal storage facilities is sent to the coal pretreatment operation where it is sized, dried and mixed with reactor product slurry recycled from the gas separation processes. The resulting feed slurry is combined with recycled hydrogen from the hydrogen/hydrocarbon recovery process and makeup hydrogen. This hydrogen-rich slurry is pumped through a preheater to the liquefaction reactor, or dissolver. Exothermic hydrogenation reactions initiated in the preheater continue in the dissolver which typically operates between $435^{\circ}C$ - $470^{\circ}C$. The reactor product slurry is sent to the gas separation processes where the gaseous products are removed. Auxilary processes separate these gases including recyled hydrogen, SNG,

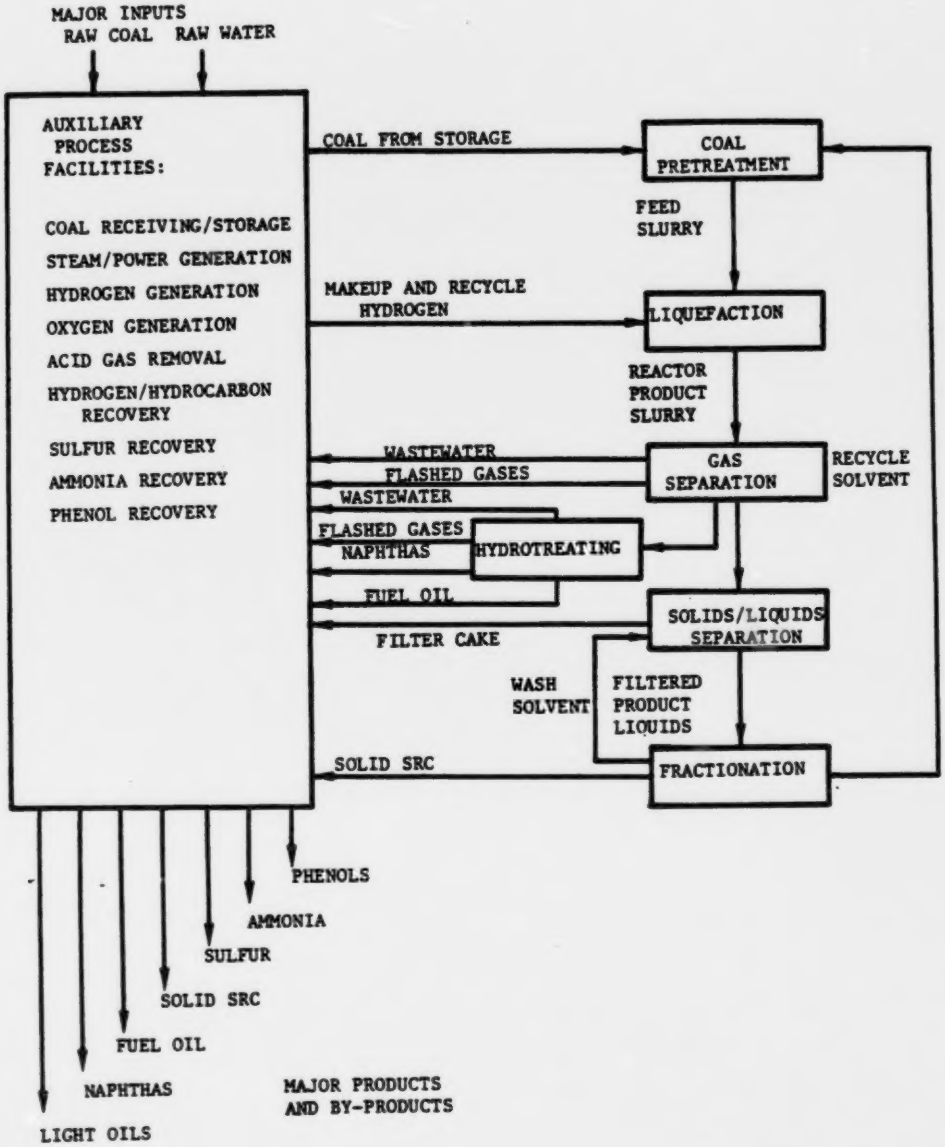
MAJOR INPUTS
RAW COAL
RAW WATER
AUXILIARY PROCESS FACILITIES:
COAL RECEIVING/STORAGE
STEAM/POWER GENERATION
HYDROGEN GENERATION
OXYGEN GENERATION
ACID GAS REMOVAL
HYDROGEN/HYDROCARBON RECOVERY
SULFUR RECOVERY
AMMONIA RECOVERY
PHENOL RECOVERY
COAL FROM STORAGE
COAL PRETREATMENT
FEED SLURRY
MAKEUP AND RECYCLE HYDROGEN
LIQUEFACTION
REACTOR PRODUCT SLURRY
WASTEWATER
FLASHED GASES
GAS SEPARATION
RECYCLE SOLVENT
WASTEWATER
FLASHED GASES
NAPHTHAS
HYDROTREATING
FUEL OIL
SOLIDS/LIQUIDS SEPARATION
FILTER CAKE
WASH SOLVENT
FILTERED PRODUCT LIQUIDS
SOLID SRC
FRACTIONATION
PHENOLS
AMMONIA
SULFUR
SOLID SRC
FUEL OIL
NAPHTHAS
LIGHT OILS
MAJOR PRODUCTS AND BY-PRODUCTS

Figure 3.1. Flow Sheet for An Integrated Liquefaction Process

LNG and sulfur species. The sulfur species are further converted to by-product elemental sulfur. Part of the separated slurry from gas separation is recycled to the coal pretreatment operation. The remainder of the slurry is sent to the fractionator. The fractionator generates three streams: a light distillate which is hydrotreated to form naphtha and fuel oil products; liquid SRC, the primary product; and a bottom stream which is sent to solids/liquids separation processes. The vacuum distillation unit in the solids/liquids separation recovers additional SRC liquid from the fractionator bottoms, yielding a residue of high mineral matter content. Part of this residue is gasified to produce makeup hydrogen.

3.2.1.1 Particulate Emissions

Fugitive emissions (i.e., particulates) will be emitted from the following sources: coal storage piles, coal reclaiming and crushing, coal receiving, dryer stack gas, and ash from stream generation. Trace elements of fugitive emissions from coal preparation have a potential health hazard consisting predominantly of aluminum, chromium and nickel (Hopkins, et al. 1978). Trace element concentrations in particulates escaping from treated stack gas are enriched in zinc, copper, zicronium, molybdenum and selenium. The trace element concentration of coal dust is expected to be similar to that of the parent coal, although certain trace elements may concentrate in the smaller size range. Dust (typically 1 to 100 μ in size) generated from coal receiving, storage, reclaiming and crushing is estimated to be about 24 tons/day for a 20,000 ton/day SRC II plant (Rogoshewski, _et al_. 1978). Table 3.1 lists analysis of some trace elements in dust from coal preparation after treatment with a wet scrubber (Hopkins, _et al_. 1978).

Suggested control alternatives for coal dust include polymer spraying, enclosed storage and water spraying. Of these, enclosed storage involves $6-8 million capital investment for a 10,000 ton coal pile (Rogoshewski, _et al_. 1978). Cyclone and baghouse filters are probably the most effective methods for controlling coal dust. Due to the small particle range, magnetic and electrostatic filters will be needed.

Table 3.1 Approximate Trace Element Analysis of Coal Pretreatment Dust after Wet Scrubbing

Element	g/day	Degree of Health Hazard*
Aluminum	8,910	2.21
Arsenic	3.9	2.50
Chromium	13.0	17.0
Nickel	15.0	1.3

*Degree of health hazard = $\frac{\text{Concentration}}{\text{MATE value}}$

3.2.1.2 Coal Pile Drainage

Coal pile runoff resulting from rainfall and such, may contain oxidation products of metallic sulfides. This runoff may also be acidic with relatively high concentrations of suspended and dissolved solids (Rogoshewski, et al. 1978). The elements in this runoff include calcium, iron, aluminum and manganese. Wastewater generated in coal preparation is routed to a thickener where particulates are removed as underflow. This underflow contains about 35% suspended solids, these solids are expected to contain the same elements as that of the original coal. Thickener underflow is mixed with coal pile runoff and sent to a tailings pond.

3.2.1.3 Gasifier Slag and Fly Ash

One of the large volume solids to be disposed of in a SRC plant is the gasifier slag and quenched fly ash. Current design specifications for the treatment of slag require that it be crushed, slurried with water and de-ashed. The fly ash from the quencher is flashed down, neutralized with lime and thickened (Hopkins, et al. 1978). It is anticipated that this waste can be disposed of in a strip mine. The leachability of this waste is one area which needs investigation.

3.2.1.4 Residue from Solids/Liquid Separation

Solid residue from solids/liquid fractionator bottoms cannot be completely utilized in hydrogen production due to its high ash content (≈ 64%). Efforts to dissolve the solid in dilute acid did not produce any leacheate. Table 3.2 gives the composition of some of the elements in this mineral residue (Hopkins, et al. 1978) which totals about 3,700 Mg/day for a SRC-II liquefaction plant producing 10,000 ton/day liquids.

Table 3.2 Estimated Trace Elements Composition of the SRC Liquefaction Residue

Element	Concentration ppm
Arsenic	24.9
Barium	579
Calcium	33,323
Iron	116,760
Luterium	2,050
Nickel	126
Sodium	1,155
Zinc	1,938

The extraction of metals from this residue is another area that requires further research.

3.2.1.5 Spent Catalyst

Catalyst used in the shift reaction in hydrogen generation has been estimated at about 135 m^3 (Hopkins, et al. 1978). Trace elements, sulfur compounds and heavy hydrocarbons may be adsorbed on the catalyst. The estimated life time of a cobalt molybdate catalyst is three years. Regeneration of spent catalyst may not be possible due to the presence of trace metals and sulfur as well as possible sintering of the catalyst. It is suggested that valuable metals be extracted from the spent catalyst at an off-site facility. Similar facilities may be needed for spent sulfur guard and methanation catalysts.

3.2.1.6 Tail Gas From Acid Gas Removal

Acid gas from the gas purification module and gas from hydrogen production are routed to a Stretford Unit where H_2S (472 Mg/day) (Hopkins, et al. 1978) is recovered as elemental sulfur. The Stretford process has an efficiency greater than 99.5% in sulfur recovery and can reduce H_2S concentrations to less than 10ppm. However tail gas treatment may be needed before the spent gas can be vented. The Stretford solution consists of mainly sodium metavanadate, sodium anthraquinone disulfonate (ADA), sodium carbonate and sodium bicarbonate in water. The Stretford solution purge stream has a total salt concentration of 10-25%. Using a high temperature hydrolysis technique, vanadium (as solid) and sodium carbonate, sulfate and sulfite can be recovered as solids. HCN is completely converted to CO_2, H_2O and N_2 (Rogoshewski, et al. 1978). The Stretford tail gas contains about 42.7% CO_2 and 5,500 ppm hydrocarbons (as C_2H_6). Direct flame incineration and carbon adsorption with incineration (AdSox) is recommended as tail gas treatment for hydrocarbons. Further scrubbing might be needed to remove CO_2 in the tail gas. It is suggested that the Stretford solution be modified to reduce CO_2 emissions in the tail gas. This is one area which necessitates further research on adsorption phenomena of SO_X and CO_2 in various solvents.

3.2.1.7 NO_X Removal

The reported sources of NO_X emissions within the SRC plant include (Hopkins, et al. 1978):

Steam generation	8.4 Mg/day
Stretford effluent gas	0.005 Mg/day

The reduction in NO_X emissions during steam generation from reducing air flow rates may not be as effective or damage-proof as other modification techniques. By supplying sub-stoichiometric quantities of primary air to burners, a 40% to 50% reduction in NO_X emissions have been observed. Another useful method of reducing NO_X is achieved by recirculation of coal flue gas which lowers peak flame temperature (Rogoshewski, et al. 1978).

Table 3.3 is a summary of some of the pollution problems associated with SRC liquefaction and suggested control alternatives.

3.2.1.8 Recommended Areas for Pollution Control Research: SRC Coal Liquefaction Process

After evaluating the available literature, the following areas are recommended for further research by the study:

Table 3-3 Pollutants and Control Options in SRC Liquefaction Process

Process	Pollutants	Sources in Process	Nature of Pollutants	Pollutant Control Strategy
Coal Pretreatment	Coal Dust	Storage, handling Sizing	Similar Original Coal	Cyclone, wet scrubbing, polymer Coating, Electrostatic and Magnetic Filters
Coal Pretreatment	Thickener Underflow	Coal Pile Run Off	Minerals and Suspended Solids	Extraction and Disposal of Tailings.
Gasifier	Slag, Fly Ash	--	Inorganics, Metals and Organics	Leaching of Metals and Strip Mining.
Solids/ Liquids Separation	Mineral Residue	Fractionator Bottoms	Inorganics, Metals and Organics	Extraction of (Toxic) Metals
Hydrogen Generation	Spent Catalyst	Reactor	--	Extraction of Co, Mo, Ni
Acid gas Removal	Tail gas	Stretford Process	Hydrocarbons and CO_2 (≈43%)	Direct Flame Incineration, Modification of Stretford process to remove CO_2
Steam Generation	NO_x Emissions	--	NO_x gases	Substoichiometric supply of air, Recirculation of Flue Gas

- The applicability of electrostatic and magnetic filters to control emissions of coal dust particles in the submicron range.
- Leachability of gasifier slag and fly ash to determine treatment and/or disposal methods.
- Extraction of possibly toxic and/or valuable metals from solids/liquids separation residue.
- Extraction of valuable metals (Ni, Co, Mo, etc.) from spent shift and hydrogen generation catalysts.
- Studies on the absorption of SO_X and CO_2 in Stretford process leading to process modification to reduce CO_2 emissions in tail gas.
- Modification of steam generation operation to reduce NO_X emissions.

3.3 GASIFICATION

In this section, the pollution problems and control alternatives for the following four High-Btu coal gasification technologies will be discussed.

1. Lurgi
2. Hy Gas
3. Bi Gas
4. Koppers-Totzek

In the following section, the Lurgi coal gasification process is discussed.

3.3.1 Lurgi Coal Gasification

The conversion of coal to SNG involves the reaction of coal with steam and oxygen in a gasifier with subsequent gas processing to (a) adjust the H_2:CO ratio by water-gas shift reaction, (b) remove acidic components, and (c) catalytic methanation. The corresponding chemical reactions are:

$$\underset{\text{coal}}{6(C{+}H)} + \frac{5}{2}O_2 + 3H_2O \rightarrow 4H_2 + 2CO + 3CO_2 + CH_4 \qquad \text{Lurgi gasification} \quad (3.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{Water-gas shift} \quad (3.2)$$

$$3H_2 + CO \rightarrow CH_4 + H_2O \qquad \text{Methanation} \quad (3.3)$$

The four major processes in the Lurgi gasification are discussed below. A flow sheet of the process is given in Figure 3.2.

3.3.1.1 Coal Preparation

Coal pretreatment in the Lurgi System generally consists of only crushing and screening the coal to produce 3-35 mm particles. This larger size range, compared to certain other gasification processes, decreases fugitive emissions.

3.3.1.2 Coal Gasification

The coal gasifier is operated at a pressure of about 25 to 35 atm and receives coal through a feed hopper at the top and discharges ash through the bottom. Oxygen and steam enter at the bottom of the gasifier and the product gas exits near the top. On a dry basis the product gas contains about 4% H_2, 3% CO_2, 18% CO and 10% CH_4 as well as higher molecular

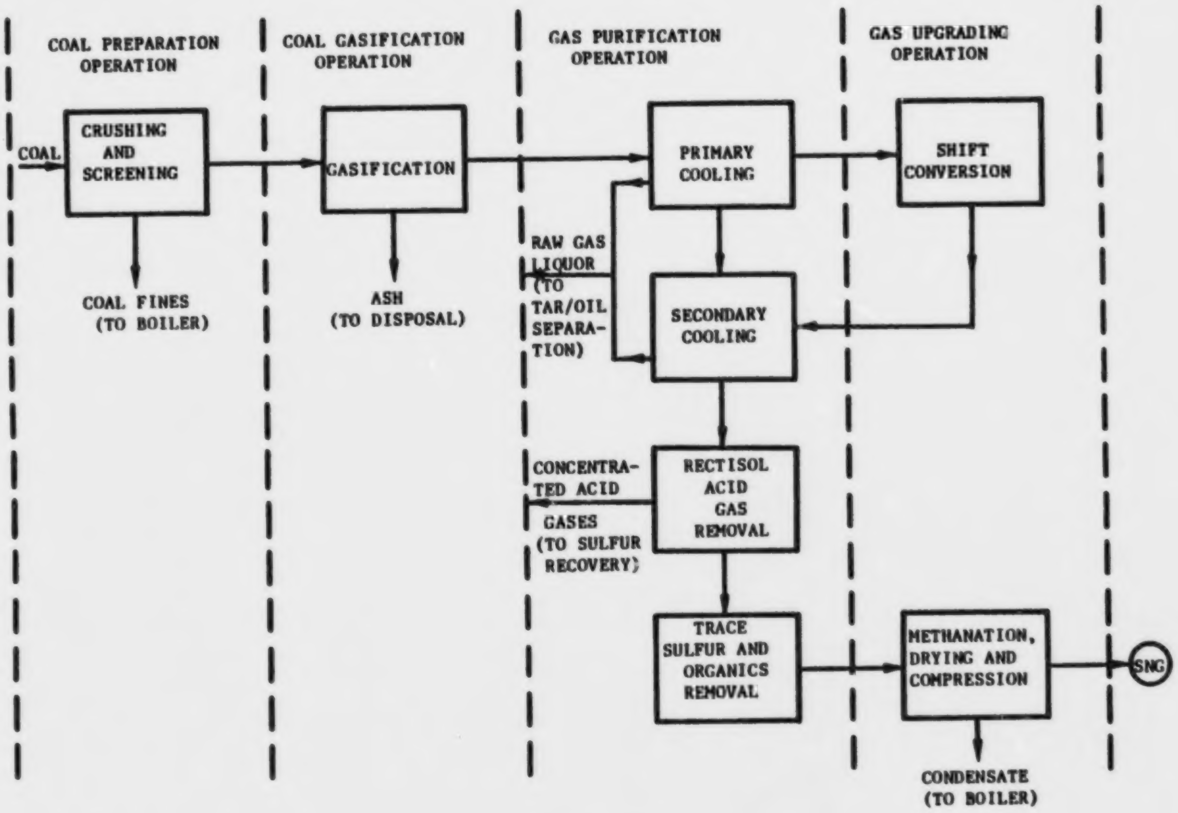
COAL PREPARATION OPERATION
COAL GASIFICATION OPERATION
GAS PURIFICATION OPERATION
GAS UPGRADING OPERATION
COAL
CRUSHING AND SCREENING
COAL FINES (TO BOILER)
GASIFICATION
ASH (TO DISPOSAL)
PRIMARY COOLING
SHIFT CONVERSION
RAW GAS LIQUOR (TO TAR/OIL SEPARATION)
SECONDARY COOLING
CONCENTRATED ACID GASES (TO SULFUR RECOVERY)
RECTISOL ACID GAS REMOVAL
TRACE SULFUR AND ORGANICS REMOVAL
METHANATION, DRYING AND COMPRESSION
SNG
CONDENSATE (TO BOILER)

Figure 3.2. Lurgi SNG Process.

weight hydrocarbons, reduced sulfur and nitrogen compounds.

3.3.1.3 Gas Purification

Gas purification consists of the removal of condensables by cooling, Rectisol treatment for the removal of bulk CO_2 and reduced sulfur compounds, and removal of trace sulfur using "methanation guards". The condensates produced are sent to tar/oil separation units and by-product recovery. The Rectisol process uses cold methanol to absorb acid gases under pressure. The used solvent is regenerated by stepwise depressurization and heating. Methanation guards are beds of solid adsorbent (e.g. ZnO). The exhausted beds are usually discarded rather than regenerated.

3.3.1.4 Gas Upgrading

Cobalt molybdate is used as shift catalyst to obtain a 3:1 H_2:CO ratio. Nickel based materials are usually used as methanation catalysts. Both the spent shift and methanation catalysts are solid wastes requiring treatment for metal recovery and/or disposal.

3.3.1.5 Gasifier and Boiler Ash

Wet ash from the gasifier and boiler ash quench systems is the largest volume solid waste stream in an SNG plant (Ghassemi, et al. 1979). A 250×10^6 Scf/day Lurgi SNG plant using a coal containing 15% ash is expected to generate about 5400 ton/day wet ash having ≈ 2% moisture content. This ash contains leachable inorganic and organic materials. These constituents can be possible sources of groundwater contamination. An alternative disposal scheme would involve stabilization to convert the wastes into a chemical form that is more resistant to leaching in the ultimate disposal site. Table 3.4 presents typical leaching study results for wastes stabilized by the Chemfix process (Connor, 1974).

Table 3.4 Laboratory Leaching Results of Chem-Fixed Refinery Wastes

Element	Concentration in Raw Sludgppm	Concentration in approx. 200 ml Leachate water after Chem Fix ppm
Total Chromium	43.5	< 0.1
Iron	1310	< 0.1
Zinc	88.0	< 0.1
Nickel	8.9	< 0.1

The leachability of the ash produced in Lurgi SNG is an area which requires further investigation.

3.3.1.6 Spent Guard Catalyst

Zinc oxide beds are used for removing the last traces of sulfur after gas removal has removed all but a few parts per million. Water vapor content is critical in that liquid water can possibly degrade the ZnO bed completely (Ghassemi, et al. 1979). The sulfur loading capacity of the ZnO catalyst increases from ≈5 wt% at 273°K to ≈ 20 wt% at 673°K.

However, the maximum recommended loading is only 3 wt% when the desired exit gas specification is 0.02 ppm H_2S (Drano Corp., 1978). Spent methanation guard material will consist primarily of zinc sulfide and unreacted zinc oxide. Operating data on the quantity and composition of spent methanation guard catalyst are needed to evaluate the disposal and/or reclamation of the spent catalyst (Ghassemi, et al. 1979).

3.3.1.7 Spent Shift/Methanation Catalysts

Catalysts used for shift and methanation require periodic replacement; the spent catalysts constitute a solid waste. Gross composition of spent catalyst is not expected to be dramatically different from that of fresh catalyst, although accumulation of carbon, sulfur, and metallic elements is to be expected. Data is needed on the characteristics of spent Lurgi SNG catalysts. Cobalt-Molybdate is used as a shift catalyst. Table 3.5 presents pilot plant data on spent Harshaw Ni-0104-T-1/4 catalyst (Leppin, 1977).

Table 3.5 Spent Harshaw Nickel Catalyst Analysis

	Typical Fresh Catalyst	Bottom of First Stage Methanator	Top of Second Stage Methanator
Sulfur, % wt.	0.15	3.7	0.16
Carbon, %	3.4	3.4	4.5
Nickel, %	60.0	52.0	61.0

Spent nickel methanation catalyst is as active as zinc for trace sulfur removal and can be used as sulfur guard catalyst (Ghassemi, et al. 1978). Sequential interchange of the first and second stage methanators is also recommended, as it is apparent from Table 3.5 that the catalyst at the top of second stage methanator is almost fresh. In the end, however, spent methanation catalyst constitutes a solid waste. The large weight percent of Ni on the catalyst would be an economic incentive for reclaiming metal from the spent catalyst. Data on the properties of spent nickel methanation catalysts and the applicability of metal extraction for reclamation are two areas that need further investigation. Further, the spent catalysts, although of small quantity, are of special concern due to their content of potentially toxic metals (Ni, Co, Mo) and coal-derived organics (metal carbonyls for example) and trace elements. Fixed-bed methanation/shift reactor system is reported to have the advantages of (1) operation at conditions removed from carbon formation, thereby increasing catalyst life, (2) reduction in catalyst sensitivity to sulfur, and (3) need CO_2 removal from a reduced volume of gas. However, this has not been commercially demonstrated yet (Gasssemi, et al. 1978).

3.3.1.8 Ash Quench Slurry

An ash quench slurry results when process waters are used to cool and transport gasifier ash to a settling unit or disposal site. No operating data are available for ash quench slurry characteristics (Ghassemi, et al. 1979). Laboratory data indicates that this slurry can contain up to 20 g/L of dissolved solids with the dominant ions being Ca^{+2}, SO_4^{-2}, K^+ and Na^+ (Griffin, et al. 1977). An increase in the solubility of Fe, Mn, Cd and Aℓ is also expected with decreasing pH. In addition, the concentration of certain hazardous elements (e.g. As, Ni, Cr and Cu) can reach levels which warrant control of the ash slurry discharge. Characterization of ash slurry water is needed to evaluate pollution control alternatives such as coagulation and flocculation of solubles.

3.3.1.9 Phenol Recovery

Gas liquor from tar-oil recovery contains a high concentration of phenols, up to 4200 mg/L (Ghassemi, et al. 1979). The Phenosolvan process using butyl acetate as solvent is used to extract these phenols. Most of the available data on the performance of this solvent extraction process are for the unit in Salsbury, South Africa. Solvents suggested for the Phenosolvan process include butyl acetate, isopropyl ether and light aromatic oil (Wurm, 1969; Earhart, et al. 1977). For butyl acetate the following distribution coefficients for various phenolic compounds have been reported (Earhart, et al. 1977).

Table 3.6 Distribution Coefficients for Various Phenols in Butyl Acetate at 300°K

Compound	K_D^*
Phenol	65
3,5 Xylenol	540
Pyrocatechol	13
Resorcinol	10

$*K_D = \frac{\text{wt. fraction in solvent phase}}{\text{wt. fraction in a aq. phase}}$, measured at high dilution

The solvents can remove only limited amounts of non-phenolic organics. A better characterization of the available solvents for phenol extraction and their removal efficiencies for various phenols are needed. Further development of solvent extraction systems to remove non-phenolic organics is also suggested.

3.3.1.10 Removal of Sulfur Compounds from Rectisol Process

In terms of total volume and content of H_2S and other reduced sulfur compounds, concentrated acid gas from the Rectisol process is the most important gaseous waste stream in a Lurgi SNG facility. Some of the control options for concentrated acid gas stream (Ghassemi, et al. 2979) are shown in Table 3.7.

Table 3.7 Control Options for the Concentrated Acid Gas Stream

Control Options	Comments
1. Claus Plant Sulfur Recovery	High Concentration of H_2S in tail gas; feed gas H_2S enrichment and Hydrocarbon removal are needed
2. Claus Plant Sulfur Recovery and tail gas treatment	Not highly effective at high levels of CO_2 in feed, applicable only for streams containing 5-15% H_2S
3. Claus Plant Sulfur recovery and SO_2 control/recovery	Reasonable option when feed gases contain more than 5-15% H_2S
4. Stretford Sulfur Recovery	Inapplicable to waste gases containing greater than 15% H_2S; not economical at high CO_2 levels; discharge may contain high COS and HC levels

The determination of the best option for the management of a specific sulfur bearing gas stream must be made on a case by case basis due to the restrictions on feed compositions and economics for different processes. Some of the above options have not appeared in commerical design (Ghassemi, et al. 1979) due to the lack of engineering data. It is suggested that research be organized to provide operational data for various sulfur recovery, SO_2 and tail gas treatment processes.

Table 3.8 summarizes some of the pollution problems associated with the Lurgi SNG process and suggested control alternatives.

3.3.2 Recommended Areas for Pollution Control Research: Lurgi Coal Gasification Process

After Evaluating the available literature, the following areas are recommended for further research by the study:

- Stabilization of gasifier and boiler ash to decrease or prevent leachability.
- Operating data and composition on spent methanation guard, shift and methanation catalyst to determine possible extraction of valuable and toxic metals.
- Studies on the use of spent methanation catalyst as sulfur guard.
- Development of solvent extraction systems to remove non-phenolic organics and determination of distribution coefficients for existing solvents.
- Engineering data on various sulfur recovery, SO_2 and tail gas pretreatment processes.

Table 3-8. Pollutants and Control Options in Lurgi SNG Process

Process	Pollutants	Sources in process	Nature of Pollutant	Pollutant control Strategy
Coal Gasification	ash	--	leachable inorganic, organic materials	stabilization of ash to decrease or prevent leach ability
Gas Upgrading	Spent methanation guard catalyst	Methanation guard reactor	ZnO with trace organics, sulfur and metals	Reclamation by extraction
Shift/Methanation	Spent catalysts	Reactors	Co, Mo, Ni, with trace organics, sulfur	Spent methanation catalyst as methanation guard, extraction of toxic metals from spent catalyst
Coal Gasification	Ash quench slurry	Thickener overflow	Dissolved inorganics, hazardous metals (As, Ni)	Coagulation and flocculation to remove dissolved salts
Tar/oil separation	Phenols in gas liquor	--	Nonphenolic organics	Better characterization of solvents to modify/develop extraction systems
Acid gas removal	Sulfur compounds	Rectisol tail gas	SO_2, H_2S, CO_2	Clans sulfur recovery and SO_2 tail gas treatment, Stretford sulfur recovery

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CHAPTER 4

EXPLOSIVES INDUSTRY

4.1 INTRODUCTION

The processes involved in manufacturing of high explosives are discussed in this chapter. The purpose of this chapter is to provide an insight in reducing the pollutants arising from these processes by means of process modification. This chapter includes the two most produced high explosives; trinitrotoluene and nitrocellulose. Both explosives are generated by nitration processes to yield nitrocompounds.

The explosive industry as a whole has been grouped into four categories:

1. Manufacturing of explosives
2. Manufacturing of propellants
3. Formulation [load, assemble and pack (LAP)]
4. Manufacturing of initiating compounds

Since both of the compounds discussed in this chapter require large amounts of nitric acid for production, the process for producing nitric acid is also presented. Process descriptions given here do not include actual formulation (load, assemble, and pack). Figure 4.1 is an overview flow chart of the explosive industry.

4.2 NITRIC ACID PRODUCTION

Figure 4.2 demonstrates the role of nitric acid in the explosive industry. The process given here is not the only

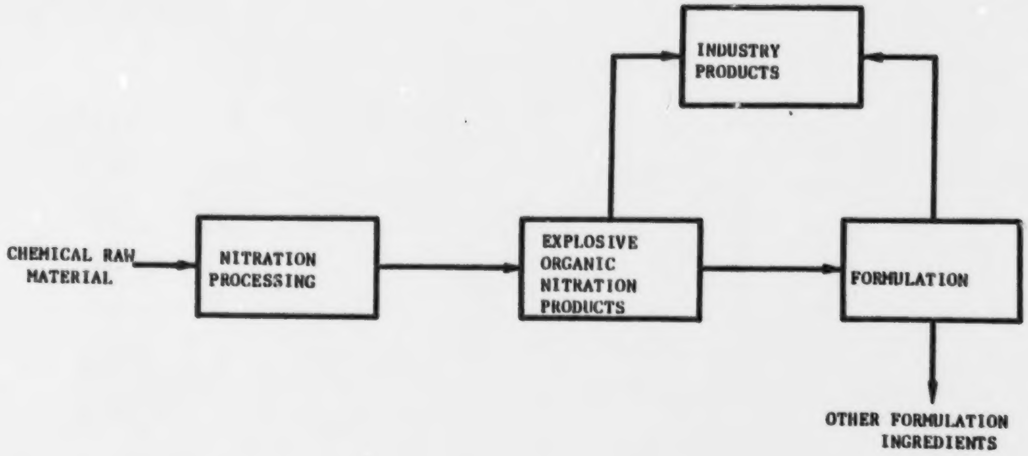
CHEMICAL RAW MATERIAL
NITRATION PROCESSING
EXPLOSIVE ORGANIC NITRATION PRODUCTS
INDUSTRY PRODUCTS
FORMULATION
OTHER FORMULATION INGREDIENTS

Figure 4.1. Processes in the Explosive Industry (Koradek and Patel, 1978).

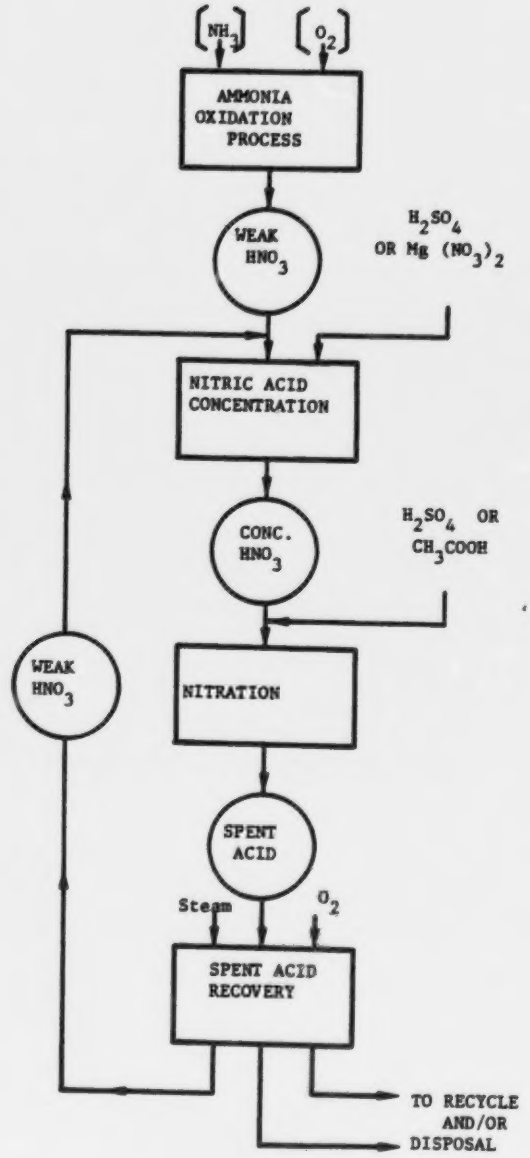
NH_3
O_2
AMMONIA OXIDATION PROCESS
WEAK HNO_3
H_2SO_4 OR $Mg(NO_3)_2$
NITRIC ACID CONCENTRATION
CONC. HNO_3
H_2SO_4 OR CH_3COOH
WEAK HNO_3
NITRATION
SPENT ACID
Steam
O_2
SPENT ACID RECOVERY
TO RECYCLE AND/OR DISPOSAL

Figure 4.2. Flow Chart for Nitric Acid Production (Hudak and Parsons, 1977).

process available for nitric acid production. As it is suggested in this section, other systems for this process must be closely examined.

4.2.1 Ammonia Oxidation Process

In this process anhydrous ammonia is vaporized and mixed with preheated air and combusted under pressure in the presence of a catalyst to produce nitric oxide. Nitric oxide is further oxidized by excess air to nitrogen dioxide and its dimer (N_2O_4). Typically the catalyst is platinum-rhubidium or platinum-palladium-mercury. The bed operates at 800-919°C and 120 psia. The equilibrium mixture of NO_2 and its dimer are adsorbed in a water cooled absorption tower to form weak nitric acid (60-65% HNO_3) (Hudak and Parsons, 1977; Patterson, et al. 1976).

The main source of pollution from the ammonia oxidation process (AOP) is the tail gas from the absorption tower which produces approximately 2.5 g NO_x/kg HNO_3 for the high pressure process. The conversion is at least 95% of theoretical with an ammonia consumption of 0.4 kg/kg HNO_3 (Hudak and Parsons, 1977). In addition, the tail gas contains N_2 (Patterson, et al. 1976).

Quantitative reduction in pollutants can be achieved as a direct result of an increase in HNO_3 production. The first strategy in increasing HNO_3 output is a more efficient design for the catalytic bed. Maximum yield of nitrogen oxides can be attained by mixing the gases via a filter near the inlet before contacting the guaze and by selection of an optimal operating temperature (Smith and Lockyer, 1979; Dorfman, et al. 1978). On the other hand, the mechanism of the surface catalysis plays an important role in NO generation. For small concentrations of NH_3 on the catalyst surface, the conversion of NH_3 into NO is almost complete. The yield of NO tends to decrease, since NO is decomposed to N_2 (Atroschenko, et al. 1979). This decrease is a result of poor exchange between catalyst surface and the gas bulk, and subsequent accumulation of NO on the catalyst surface. Based on this argument, the yield of NO in the bed can be optimized by increasing the rate of mass transfer from the bulk gas to the catalyst surface. Furthermore, the degree of dissociation of NO increases linearly with time (Zhidkov, et al. 1979). Thus knowledge of the NO dissociation reaction and NO production rate will be needed in maximizing NO output.

It is also of value to examine the operating parameters for the absorption tower. The rate of nitric acid production can be improved by controlling the temperature of the absorber. Dorfman, et al. (1978) accomplished a 4% increase in HNO_3 output by adjusting the H_2O consumption, thus controlling the temperature.

4.2.2 Nitric Acid Concentration

The nitric acid concentration process is a continuous operation in which nitric acid from the AOP is mixed with concentrated H_2SO_4 and fed to the distillation tower with steam. The sulfuric acid combines with free water while HNO_3 vapors (98-99%) (Hudak and Parson, 1977) form an overhead stream. The nitric acid vapors, contaminated with small amounts of NO_x and O_2 from HNO_3 dissociation, pass to a bleacher and condensor. The HNO_3 vapors condense as 95-99% HNO_3, while NO_x and O_2 pass to the absorber column for conversion to and recovery of additional weak nitric acid. This weak nitric acid is recycled to the dehydrating unit. The bottom product, consisting of approximately 68% H_2SO_4 (Hudak and Parsons, 1977), is recovered and sent to a concentration unit for reprocessing.

The principle source of emissions, 0.1 - 2.5 g NO_x/Kg HNO_3 produced (Hudak and Parsons, 1977), is from the absorber tail gas. The NO_x content of the tail gas is affected by several variables: insufficient air supply to the absorber, high temperatures in the absorber, and internal leakage which permits gases from the AOP to enter the absorber (Hudak and Parsons, 1977).

In search of process modifications which may lead to abatement of pollutants, it is advantageous to consider other processes for production of nitric acid. One such newly developed process is concentrating nitric acid by surpassing the azeotrope. In this process the gases leaving the oxidation step of AOP are enriched in NO_2 and then absorbed in azeotropic acid to produce a super azeotrope mixture (80% HNO_3). This mixture is then easily distilled. The exiting gases from this particular process contain 300 ppm of NO_x (Marzo and Marzo, 1980). The advantage of this process as opposed to the conventional, oxidation absorption operation, should be considered.

4.2.3 Spent Acid Recovery

Spent acid from the various nitration processes flow into the top of a denitrating tower. The HNO_3 and NO_x are stripped from the spent acid by steam. The bottom product contains H_2SO_4 which is sent to a H_2SO_4 concentrator. Sulfuric acid (93%) from the concentrator is a by-product of most nitration processes (Patterson, et al. 1976).

Waste waters from the spent acid recovery unit are characterized by high concentrations of suspended solids and small quantities of nitrogen salts. The solids from these processes, called nitrobodies, must be removed from the spent acid for pollution control.

Table 4.1 summarizes some of the pollution problems associated with nitric acid production and suggests the control alternatives.

4.2.4 Recommended Areas for Pollution Control Research in Nitric Acid Production

After evaluating the available literature, the following areas are recommended for further research by the study:

Table IV-1 Pollutants and Control Options in Nitric Acid Production Process

Process	Pollutants	Source in Process	Nature of Pollutants	Pollutant Control Strategy
Ammonia Oxydation Process	NO_x, N_2	Tail gas from absorption tower	Inorganic gases	Adjustment of operating temperature for maximum HNO_3 output. Mixing of gases at the inlet of catalytic bed. Improvement of mass transfer rate between the catalyst and the bulk gas.
Nitric acid concentration	NO_x	Absorption tail gas	Inorganic gases	Provide sufficient air supply. Prevention of leakage from AOP.
Spent acid recovery	Nitrogen salts nitrobodies	From nitration processes.	Organic and inorganic	Removal of suspended solid

- Studies on kinetics and mass transfer process for heterogeneous catalysis to improve the catalytic bed design which will reduce NO dissociation and increase NH_3 consumption.
- Studies on heat and mass transfer with reaction in absorption towers to optimize HNO_3 production by finding the optimal parameters for adsorption tower operation.
- Consideration of nitric acid production by means of a super azeotropic mixture which may be useful in modification of the present process.

4.3 TNT PRODUCTION

Trinitrotoluene is the most extensively produced military high explosive. Production of TNT during 1969-71 exceeded 22,000 tons/month, more than any other high explosive compound (Patterson, _et_ _al_. 1976). Trinitrotoluene production involves three distinct processes, nitration, purification and finishing. Schematically, TNT production is shown in Figure 4.3.

4.3.1 Nitration

Nitration of toluene is performed in a series of reactors with a mixed acid stream flowing countercurrently to the flow of the organic stream. The oleum fed to the last reactor emerges as the spent acid from the first reactor. The acid stream to second and third reactors are fortified with 60%

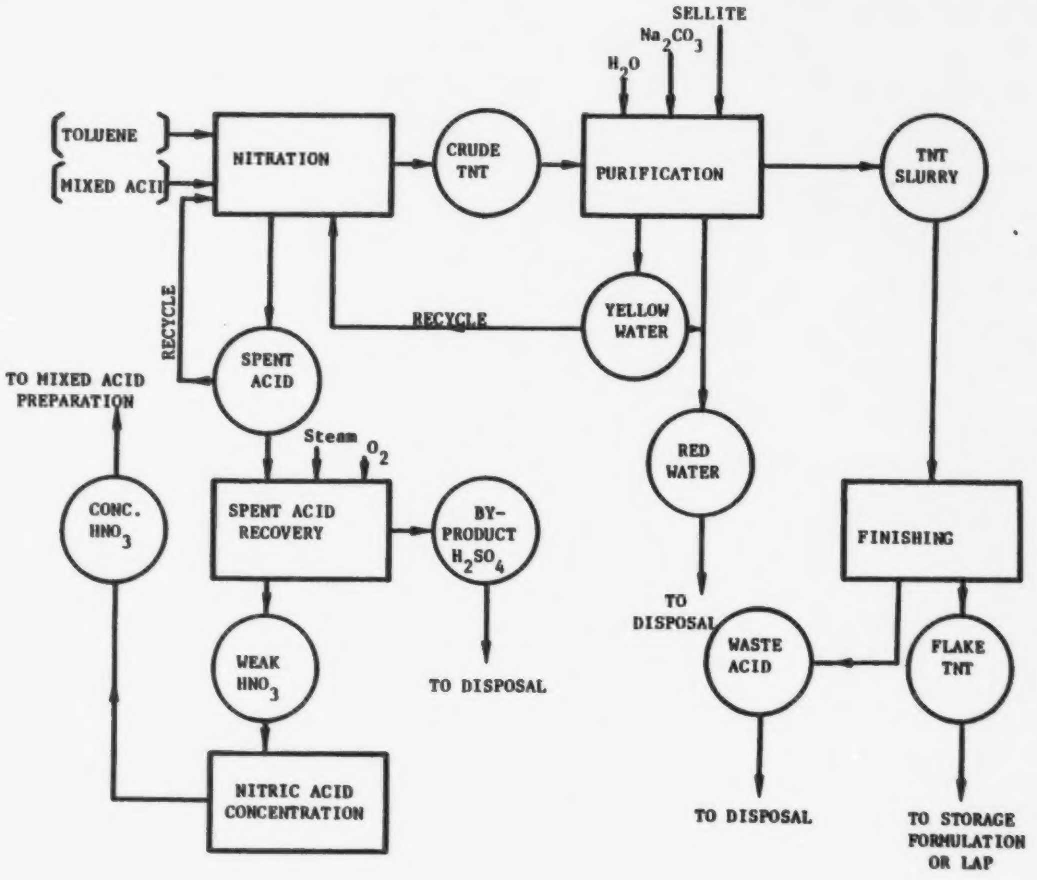
TOLUENE
MIXED ACID
NITRATION
CRUDE TNT
H$_2$O
Na$_2$CO$_3$
SELLITE
PURIFICATION
TNT SLURRY
RECYCLE
RECYCLE
YELLOW WATER
SPENT ACID
TO MIXED ACID PREPARATION
Steam
O$_2$
RED WATER
CONC. HNO$_3$
SPENT ACID RECOVERY
BY-PRODUCT H$_2$SO$_4$
FINISHING
TO DISPOSAL
WEAK HNO$_3$
TO DISPOSAL
WASTE ACID
FLAKE TNT
NITRIC ACID CONCENTRATION
TO DISPOSAL
TO STORAGE FORMULATION OR LAP

Figure 4.3. Flow Chart for TNT Production (Hudak and Parson, 1977).

HNO_3. "Yellow water" is added to the second reactor. Approximately 5% (Hudak and Parsons, 1977; Patterson, et al. 1976) of the TNT from the third reactor is β or 2,3,4 and γ or 3,4,6 isomers (the favorable product is α or the 2,4,6 isomer).

The gases from the nitrator-separator step contain CO, CO_2, NO, NO_2, N_2O and trinitromethane (TNM). These gases are passed through a fume recovery system, for recovery of NO_x as nitric acid, and are then vented through a scrubber to the atmosphere. Final emissions contain unabsorbed NO_x as well as TNM. Rated capacity for a typical fume recovery system operation for the continuous process is indicated to be 272 Kg HNO_3/hour (Hudak and Parsons, 1977). Approximately 245 Kg NO_x/Mg TNT are generated by the nitrators of which 9.6 Kg NO_x/Mg TNT are vented to the atmosphere (Hudak and Parsons, 1977). In addition unsymmetrical "meta" isomers as well as oxidation products are generated. "Red Water", the main source of pollution, is the by-product of the treatment of "meta" isomers in the purification step.

The pollutants from TNT production can be alleviated by improving the chemical reaction that would decrease the decomposition of nitric acid, the oxidative side reactions, and the formation of unsymmetrical isomers. For this purpose a low temperature (-10°C) nitration, dinitrate toluene, followed by a high temperature (90°C) trinitration is recommended (Hill, et al. 1976; Haas, et al. ____). The major changes from the existing process occur in the dinitration step. It was shown that lowering the temperature from 33°C to -8°C in the dinitrator step results in reduction of "meta" isomers concentration in the product from 2.4% to 1.8% (Haas, _et al_. ____).

The fume recovery system for gaseous emissions in the nitration separation step must be designed to operate efficiently at the maximum production level of TNT.

4.3.2 Purification

The crude TNT from the nitration step is washed with water to remove free acids. This step is accomplished by using a countercurrent flow of water. The TNT is then neutralized with soda ash and treated with a 16% aqueous sodium sulfite (sellite) solution to remove the nitro group in the meta position is α and γ - TNT by a sodium sulfonate group, forming highly soluble sodium salts of the corresponding dinitrotoluene sulfonic acid. The TNT is then treated in a series of countercurrent extractors with H_2O and is then transferred to the finishing process as a slurry.

The waste stream from the purifications are "yellow water", "red water" and "pink water". "Yellow water" is generated as a result of the first water wash. Some of this acidic effluent is returned to the dinitration step and the rest is combined with other process waste waters for treatment. "Red water", the effluent of sellite treatment and subsequent washing of TNT, is composed of 27.6% water, 17.3% organics, 5.2% $NaNO_x$, and 2.9% Na_2SO_x (Hudak and Parsons, 1977). The generation of "red water" amounts to 0.34 kg/kg TNT produced and consists of 0.26 kg process water, 0.06 kg organics (nitrotoluenes and nitrotoluene - sulfonic acid salt), and .02 kg dissolved organics ($NaNO_x$ and $NaSO_x$) (Hudak and Parsons, 1977). "Pink water" is the waste stream generated from TNT manufacturing as well as LAP operation. "Pink water" arises from the nitration fume scrubber discharge, "red water" concentration distillate, finishing operation hood scrubber and wash down effluent, and possibly spent acid recovery wastes.

Control strategy for reduction of "red water" has been discussed in the nitration section.

The traces of TNT in "pink water" and "yellow water" should be recovered. It is possible to purify these streams by treating the waste waters with surfactant, thus forming a precipitate with TNT which can easily be removed by filtration (Okamota, et al. 1979). The "pink water" resulting from TNT spent acid recovery contains 15-118 kg/day of TNT for a typical plant (Hudak and Parsons, 1977). In addition "pink water" contains DNT which, by imporving the nitration process, should be reduced to a tolerable level.

4.3.3 Finishing

In this process TNT is solidified on a water-cooled flaker drum or belt and is then scrapped with a blade.

The waste stream from the finishing process is mainly waste from spillage, floor drainage, and washings from the finishing area.

The recovery of TNT from these waste streams should be considered if TNT appears in any large quantities in these streams.

Table 4.2 is the summary of the pollution problems associated with TNT production and suggested control alternatives.

4.3.4 Recommended Areas for Pollution Control Research in TNT Production

After evaluating the available literature, the following areas are recommended for further research by the study:

- Research on kinetics of the nitration reactions which will permit alleviation of pollutants by adoption of a low temperature denitration stage.
- Material balances to find the optimal design for the fume recovery system in the nitration-separation process.
- Recovery of TNT in the "pink water" by application of foam separation to an aqueous solution.

4.4 NITROCELLULOSE PRODUCTION

Nitrocellulose (NC) is the second largest product from the military sector of the U.S. explosive industry, with a 1969-71 production level of nearly 12,400 tons/month (Patterson,

Table 4-2 Pollutants and Control Options in TNT Production

Process	Pollutants	Sources in process	Nature of pollutants	Pollutant control strategy
Nitration	CO, CO_2, NO, NO N_2O, NO_x TNM unsymmetrical "Meta" isomers of TNT	Nitrator-Separator	Inorganic and organic, gases	Low temperature dinitration stage to reduce "meta" isomers and oxides of nitrogen and carbon.
		Fume recovery system	Inorganic and organic gases	Change the design as to operate at maximum TNT production capacity
Purification	"Yellow water" acidic effluent traces of TNT	First water wash	Inorganic and organic liquid	Removal of TNT from all waste waters by application of foam separation. "Red water" generation will be considerably lower when "meta" isomers formation is decreased.
	"Red water" $NaNO_x$, Na_2SO_x nitrotoluenes and nitrotoluenes sulfuric acid	Sellite wash	Inorganic and Organic liquids	
	"Pink water" DNT, TNT, all pollutants present in red water	Nitration fume scrubber discharge "Red water" concentration distillates. Finishing operation hard scrubber Wash down effluent	Inorganic and organic liquid	
Finishing	Spillage, drainage.			

et al. 1976). NC is the fundamental ingredient used in the production of all gun propellants and many rocket propellants. Cellulose mononitrate, dinitrate and trinitrate have nitrogen contents of 6.75, 11.11, and 14.4% respectively, representing progressive replacements of the -OH groups in the cellulose unit by ONO_2 groups. Typically there are three grades of NC; proxylin, pyrocellulose, and guncotton with 8-12%, 12.6%, and 13% minimum nitrogen content respectively. The preparation of all grades of NC require the same procedure with the exception of the acid mix used in the nitration process (Mark, 1966). Manufacturing of NC consist of two processes, nitration and purification. An overall flow chart of NC production is depicted in Figure 4.4.

4.4.1 Nitration

In this process, pre-purified pulp is added to a mixture of nitric acid and sulfuric acid in "dipping pots". Since the nitration reaction is exothermic the vessel is cooled, the operating temperatures vary from 30 to 34°C as well as 37 to 40°C. In a continuous process approximately 68 to 70 kg/min of crude NC is produced.

The nitration is followed by centrifuging the crude NC to remove spent nitrating acids. The wrung NC is then dumped into "drowning tubs" filled with water to stop the reaction. The nitrogen content of NC is held between 10.5% to 13.8% nitrogen (Hudak and Parsons, 1977).

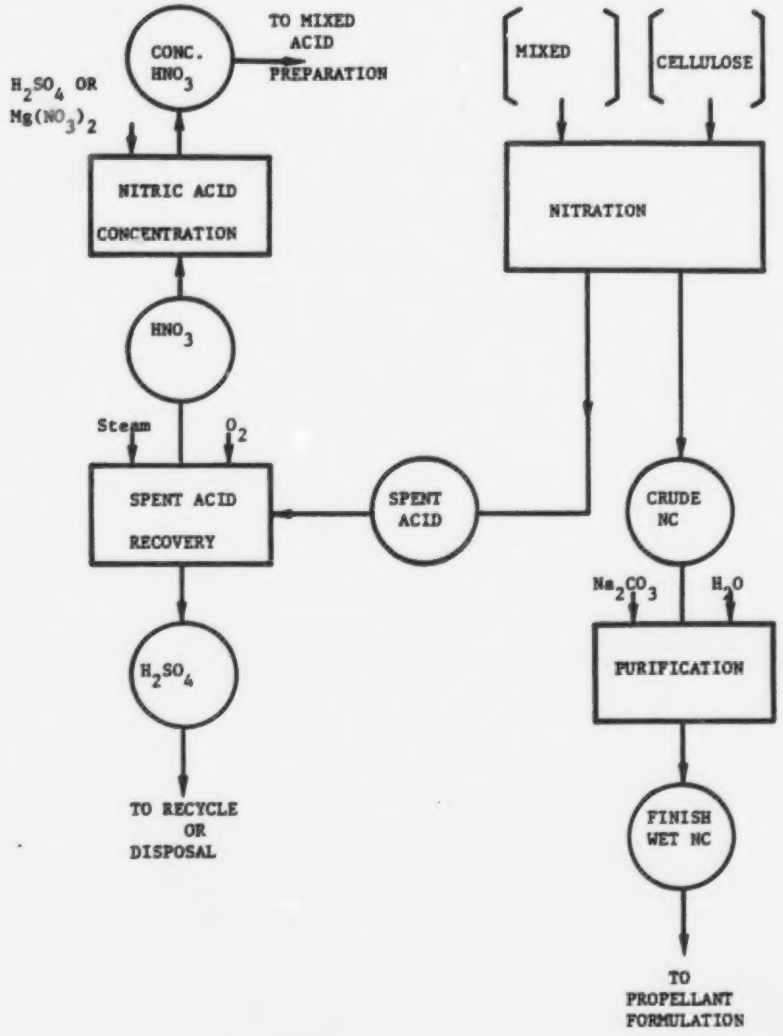
CONC. HNO3
TO MIXED ACID PREPARATION
H2SO4 OR Mg(NO3)2
NITRIC ACID CONCENTRATION
HNO3
Steam
O2
SPENT ACID RECOVERY
SPENT ACID
H2SO4
TO RECYCLE OR DISPOSAL
MIXED
CELLULOSE
NITRATION
CRUDE NC
Na2CO3
H2O
PURIFICATION
FINISH WET NC
TO PROPELLANT FORMULATION

Figure 4.4. Flow Chart for Nitrocellulose Production. (Hudak and Parsons, 1977).

The pollutants emitted from the nitration process are 0.65g SO_x and 1.05g NO_x per kg NC from the reactor pots and 32.5g SO_x and 14.5g NO_x per kg NC from the acid concentrators. The NO_x from the reactors and centrifuge are vented to an absorber where NO_x is oxidized and absorbed in the water generated weak nitric acid. Most of the waste water from nitration process is due to clean ups. Thus, waste waters may be expected to have a low pH, relatively high levels of NO_3, and suspended solids.

Nitration of cellulose in the "dipping pots" can be formed at 17 to 45°C (Miles, 1955), depending on the nature of the desired product. Julian Linares (1966) carried out this nitration at 29°C producing cellulose nitrate of 13.35% N content. Thus, it is evident that the nitration temperatures are flexible and can result in an end-product of comparable quality. The optimal operating temperature must be considered for reduction of SO_x and NO_x emissions. Furthermore, the possibility of converting the waste acid from the nitration process to sulfuric acid must be considered. Such a process involves the reaction of roasting gases containing SO_2 at temperatures exceeding 250°C with the acid waste (mostly H_2SO_4 and HNO_3) and water spray to form sulfuric acid (Rensh and Jenthe, 1967). Absorption of NO_x from the acid concentrator also may prove beneficial.

4.4.2 Purification

The purification of NC invloves five processes: boiling tub house, beater house, poacher house, blender house, and final wringer house. In the boiling tub house, unstable sulfate esters and nitrates of partially oxidized cellulose are destroyed by acid hydrolysis. In the beater house, the NC is reduced to a physical state more amenable to purification by Jordan beaters. In the poacher house the NC is treated with soda ash and unpulped fibers are removed. The function of the bleacher house is to sample and regulate the quality of the final product. In the final wringer house, the NC slurry is centrifuged to approximately 30% moisture content.

Due to large quantities of process water used during the manufacturing of NC, the treatment and disposal of waste water is a formidable problem. Presently, overflow from the settling pits flows to the waste acid neutralization facilities where $CaCO_3$ is added to neutralize the acid. After neutralization, the material is either discharged directly or transferred to settling lagoons. Approximately 13.6×10^6 kg $CaSO_4$ sludge is generated yearly, as a result of waste acid neutralization, at one NC production plant (Hudak and Parsons, 1977).

Waste waters from the beater, poacher and blender houses flow to another pit area where NC fines settle out. Effluent from the pit is either recycled to the wash lines or is discharged. The major portion of total suspended solids in the waste water discharged, is NC fines. One source lists the following losses during NC purification (Hudak and Parsons, 1977):

Boiling tub house	68.2 kg/day
Jordan beater house	295 kg/day
Poacher house	295 kg/day

Nitrocellulose fines lost during the boiling tub, Jordan beater, and poacher house operations constitute inefficiencies in NC Purification. NC fines can be recovered from waste waters by simple filtration, thus reducing the suspended solid content as well as improving the efficiency of the process.

It is perhaps, not possible to recycle all the water used in the purification of NC, but it may be possible to reduce the volume of the waste water. For this purpose an in-depth study of NC purification is necessary. Such studies must concentrate on methods of purification with minimum water usage. Thus, an overall material balance of the purification step will be useful.

Table 4.3 is a summary of the pollution problems associated with NC production and suggested control alternatives.

4.4.3 Recommended Areas for Pollution Control Research in Nitrocellulose Production

After evaluating the available literature, the following areas are recommended for further research by the study:

- Better understanding of the kinetics of the cellulose nitration will indicate methods of

Table 4-3. Pollutants and Control Options in NC Production

Process	Pollutants	Source in process	Nature of pollutant	Pollutant Control Strategy
Nitration	SO_x, NO_x, NO_3 suspended solid	Reactors, nitration vessel.	Inorganic gases and solid.	Improve reaction by temperature adjustment to reduce generation of oxides.
	Waste acid HNO_3, H_2SO_4	Centrifuge	Inorganic acids	Conversion to sulfuric acid by spraying acid waste by water in presence of roasting gases containing SO_2.
Purification	NC fines	Boiling Tub house Jordan beater house poacher house	Organic, suspended solids	Removal by filtration from waste streams.
	Process water, acidic.		Inorganic acids	Reduction of process water.

operation to minimize NO_x and SO_x formation.

- Better understanding of absorption of SO_x and addition of an absorption tower to the acid concentrator to recover NO_x.
- Research on filtration operations and filtration units for effective recovery of NC fines from boiling tub, Jordan beater and poacher houses.
- Reexamine and modify flow streams to optimize water usage by recycle and other techniques in the purification process.

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CHAPTER 5

IRON AND STEEL INDUSTRY

5.1 INTRODUCTION

The manufacture of steel involves many processes which require large quantities of raw materials and other resources. Due to the wide variety of products and processes, operations vary from plant to plant. However, the steel industry can be segregated into two major components; raw steel making, and, forming and finishing operations. An overview of the iron and steel process is given in Figure 5.1 (U.S. EPA, Dec. 1980a).

In the first major process, coal is converted to coke. Nearly all active coke plants are by-product plants which produce, in addition to coke, usable by-products such as coke oven gas, coal tar, crude or refined light oils, ammonium sulfate or anhydrous ammonia, and napthalene. Less than 1% of domestic coke is produced in behive coke making.

The coke from coke making operations is then supplied to the blast furnace process where molten iron is produced. In the blast furnaces, iron ore, limestone and coke are placed into the top of the furnace and air is blown countercurrently from the bottom. The combustion of coke provides heat which produces metallurgical reactions. The limestone forms a fluid slag which combines with unwanted impurities in the ore. Molten iron from the bottom of the furnace and molten slag, which floats on top of the iron, are periodically withdrawn.

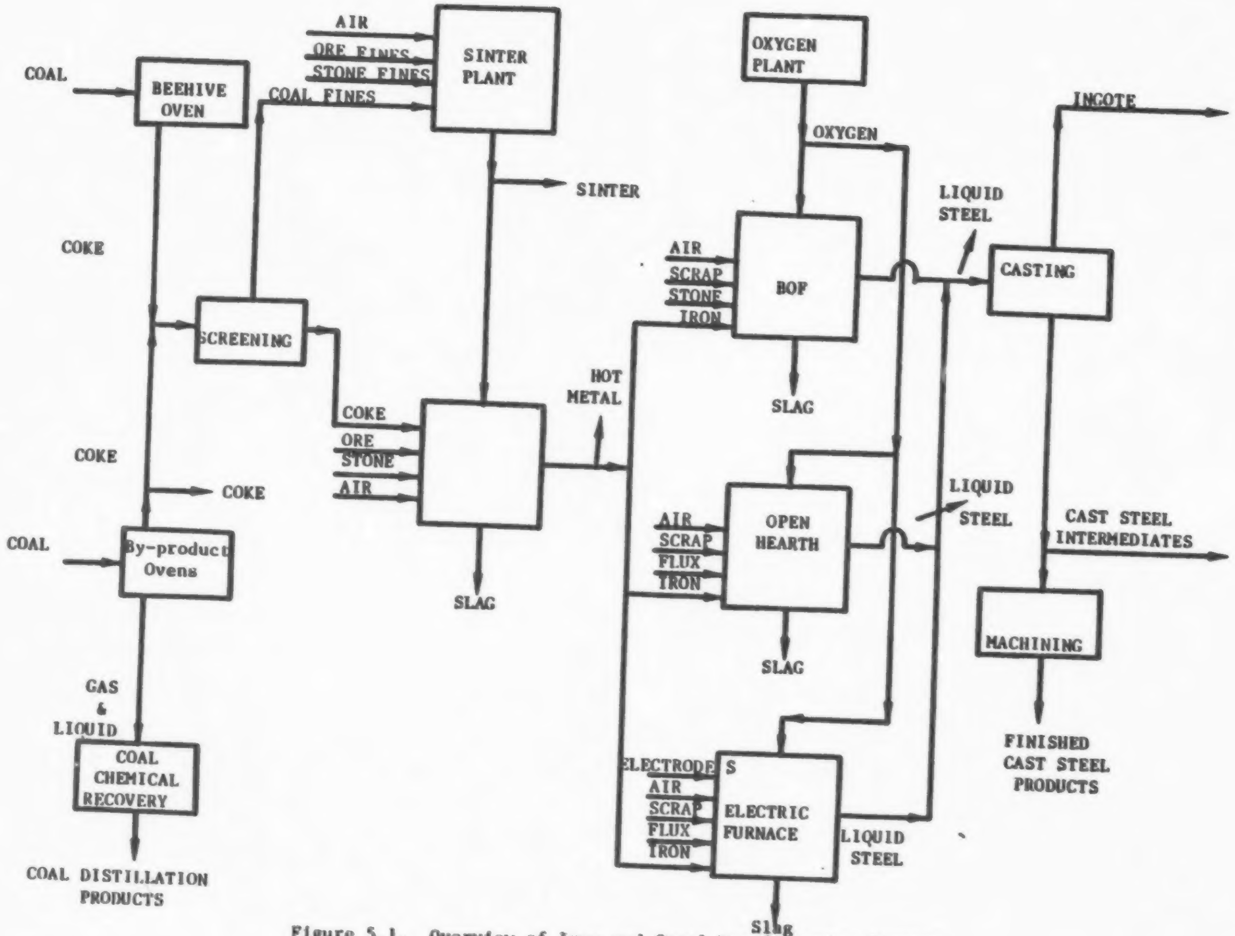
COAL
BEEHIVE OVEN
COKE
SCREENING
COKE
COKE
COAL
By-product Ovens
GAS & LIQUID
COAL CHEMICAL RECOVERY
COAL DISTILLATION PRODUCTS
AIR
ORE FINES
STONE FINES
COAL FINES
SINTER PLANT
SINTER
COKE
ORE
STONE
AIR
SLAG
HOT METAL
OXYGEN PLANT
OXYGEN
AIR
SCRAP
STONE
IRON
BOF
SLAG
AIR
SCRAP
FLUX
IRON
OPEN HEARTH
SLAG
ELECTRODES
AIR
SCRAP
FLUX
IRON
ELECTRIC FURNACE
Slag
LIQUID STEEL
LIQUID STEEL
LIQUID STEEL
CASTING
INGOTE
CAST STEEL INTERMEDIATES
MACHINING
FINISHED CAST STEEL PRODUCTS

Figure 5.1. Overview of Iron and Steel Manufacturing Process

The blast furnace flue gas, which has considerable heating value, is cleaned and then burned in stoves to preheat the incoming air blast to the furnace.

Steel is an alloy of iron containing less than 1% carbon. Steel making consists essentially of oxidizing constituents (particularly carbon) at specified low levels, and then adding various alloying elements according to the grade of steel to be produced. The basic raw materials for steel making are hot metal SV pig iron, steel scrap, limestone, burned lime, dolomite, fluorspar, iron ores, and iron-bearing materials such as pellets or mill scale. The principle steel making processes in use today are the Basic Oxygen Furnace (BOF), the Open Hearth (OH) Furnace, and, the Electric Arc Furnace (EAF).

The hot forming (including continuous casting) and cold finishing operations follow the steel making process. These operations are so varied that simple classification and description is difficult. In general, hot forming primary mills reduce ingots to slabs or blooms and secondary hot forming mills reduce slabs or blooms to billets, plates, etc. Steel finishing operations involve a number of operations that basically impart desirable surface or mechanical properties to the steel. Correct surface preparation is the most important requirement for satisfactory application of protective coatings to the steel surface. The steel surface must be cleaned at various production stages to insure that the oxides which form on the surface are not worked into the finished product. The pickling process, chemically removes oxides and scale from the surface of the steel by the action of inorganic acids. This method is the most widely used due to comparatively low operating costs and ease of operation. Pickling will be the only finishing operation considered in this report.

5.2 COKE MAKING

Figure 5.2 provides a flow diagram of a coke plant, the processes required include:

1. Coal Mining and Transportation
2. Coal Preparation
3. Charging of Coal
4. Coking
5. Pushing and Quenching
6. Coke Handling and Tar Condensation

Coal dust is emitted during size reduction and transportation of the coal. Emissions are estimated to be 5 kg/yr/ton of coal. Particles are generally less than 0.1 mm in size with suspended fractions in the range of 1 to 10 µ (Barnes, et al. 1970). The wastewaters produced from coal preparation may contain up to 200 g/l of suspended particles (28 mesh to colloidal dimensions) and most can be eliminated by thickeners, cyclones and filters (Keystone Coal Industry Manual, 1974). Some trace elements contained in the wastewater include arsenic, cadmium and lead.

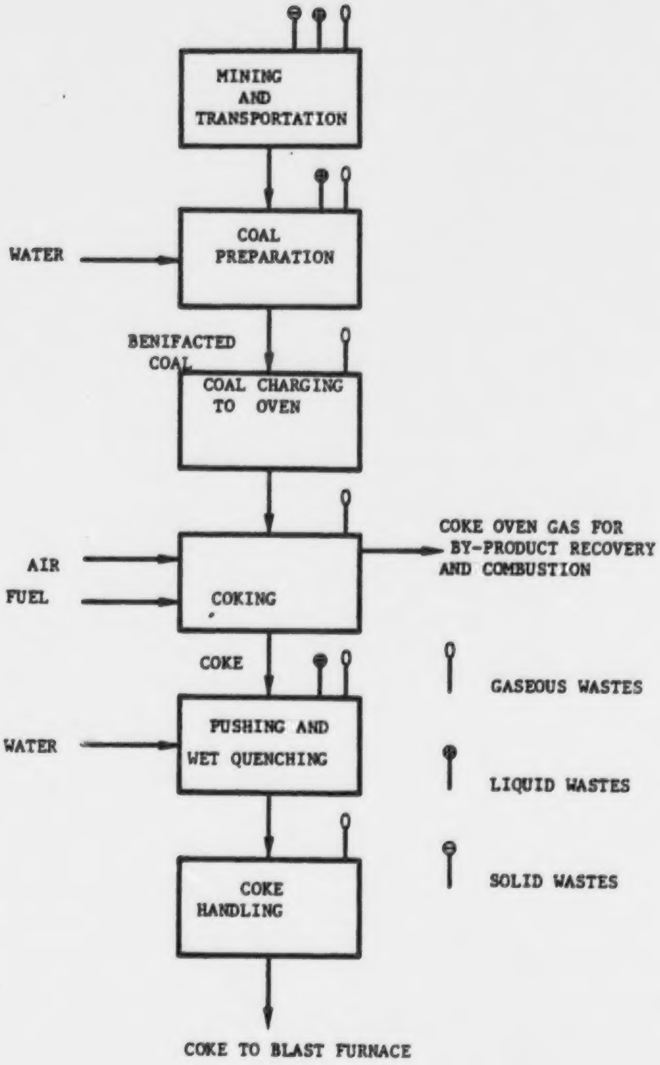
MINING AND TRANSPORTATION
WATER
COAL PREPARATION
BENIFACTED COAL
COAL CHARGING TO OVEN
AIR
FUEL
COKING
COKE OVEN GAS FOR BY-PRODUCT RECOVERY AND COMBUSTION
COKE
WATER
PUSHING AND WET QUENCHING
COKE HANDLING
COKE TO BLAST FURNACE
GASEOUS WASTES
LIQUID WASTES
SOLID WASTES

Figure 5.2. Coke Making

Coke is the residue from the destructive distillation of coal. Coal is heated in the coke ovens (with no air in the oven) by adjacent chambers or flues using; 1) some of the gas recovered from coking operations, 2) cleaned blast furnace gas, or, 3) a mixture of coke oven and blast furnace gases. During carbonization about 20% to 35% by weight of the initial coal charge is evolved as mixed gases and vapors which are collected through an opening at the top of the oven. From one ton of coke about 544-634 kg blast furnace coke, 45-91 kg coke breeze, 270-325 m^3 coke oven gas, 30-45 kg tar, 9-13 kg $(NH_4)_2SO_4$, 54-312 kg ammonia liquor and 9-15 kg light oil are produced (Keystone Coal Industry Manual, 1974). Potentially hazardous emissions from a coke plant include CO, amines, organometallics, tar and soot, carbonyls, hydrogen cyanide, sulfur compounds, etc. (Cavanaugh, *et al*. 1974). The use of refined or cleaned coal as a raw material and better knowledge of coking reactions can eliminate or reduce some of these pollutants.

Most of the particulates generated in hot coke quenching operations are collected and reused within the plant and do not constitute a significant pollution problem. However, wastewaters from wet coke quenching operations contain high concentrations of ammonia, oil and grease, and phenol (all of the three exert a biochemical oxygen demand), plus cyanide, sulfide and suspended solids. Table 5.1 gives an analysis of quench wastewater samples (U.S. EPA, Feb. 1977).

TABLE 5.1 AVERAGE ANALYSIS OF QUENCH WATER SAMPLES

Contaminants	Concentration (ppm)
Phenols	776
Sulfates	1,066
Chlorides	1,954
Total Ammonia	2,517
Cyanides	98
Total Solids	5,214

Some of the treatment technologies used for control of pollution from the quench waters are (U.S. EPA, Jan. 1974):

1. Distillation With Ammonia Recovery of Waste Ammonia Liquor
2. Alkaline Ammonia Stripping
3. Neutralization
4. Settling
5. Air Flotation
6. Clarification With Vacuum Filtration of Sludge
7. Filtration
8. Carbon Adsorption

Conversion of hot coke quenching from the wet to the dry process would: 1) eliminate air and wastewater emissions from the wet quenching process, 2) provide additional potential for particulate emission since control of these emissions are part of the the dry quenching design (U.S. EPA, July 1976). Pollution control costs are not significant for the dry process. The hot quench gases can be cooled recovering useful energy. Capital and operating costs are significantly higher than wet quenching operations by up to 10.7 dollars per ton of coke. Dry coke quenching is claimed to produce a higher-grade coke by Russian authors, thus reducing the coke rate in the blast furnace. However, this claim needs to be demonstrated for U.S. coals.

A detailed description of the dry coke quenching process is given in "Environmental Considerations of Selected Energy Conserving Manufacturing Process Options." In dry quenching of coke, the hot coke pushed from the ovens is cooled in a closed system. Dry quenching uses "inert" gases to extract heat from the incandescent coke by direct contact. The heat is then recovered in waste heat boilers or by other techniques. The "inert" gases can be generated from an initial intake of air which reacts with the hot coke to form a quenching gas containing 14.5% CO_2, 0.4% O_2, 10.6% CO, 2% H_2 and 72.5% N_2. After cooling, the gases pass through two dust recovery cyclones (where particulates are collected at ~400-600 lb/hr.) before being recycled. The particulates consist mainly of carbon dust and is burnt as solid fuel. Part of the gases after particulate removal may be sent for removal of evaporated cyanides and SO_x, to prevent accumulation. Additional research is needed to study the applicability of dry quenching of U.S. coals and the cleaning of recycle gases using systems similar to those used in by-product coke recovery operations, as discussed below.

5.3 COKE BY-PRODUCT RECOVERY

Figure 5.3 shows the various coke by-product recovery operations (U.S. EPA, Feb. 1977).

The condensate from the cooled coke oven gases contains tar and ammonia liquor which are decanted. The uncondensed gases are reheated and passed on to the ammonia scrubber. Some of the tar derivatives recovered include creosote oil, cresols, naphthalene, phenol and medium and hard pitch. Phenol is recovered from the weak ammonia liquor by scrubbing with benzene or light oil. The phenolized benzene or light oil is contacted with caustic soda to extract sodium phenolate. The sodium phenolate is neutralized with CO_2 to liberate crude phenols.

The weak ammonia liquor is heated to remove "free" ammonia and is then contacted with $Ca(OH)_2$ solution to remove and strip NH_3 as vapor. These vapors are sent to the ammonia absorption process. The waste liquor generated in the ammonia still contains 0.75 of sulfide as H_2S. The total amount of waste produced ranges between 80-340 tons of coal carbonized. These wastes may contain up to 20% by volume of $Ca(OH)_2$ (U.S. EPA, Feb. 1977). It is suggested that $Ca(OH)_2$ be recovered from the waste liquids and recycled to the ammonia still.

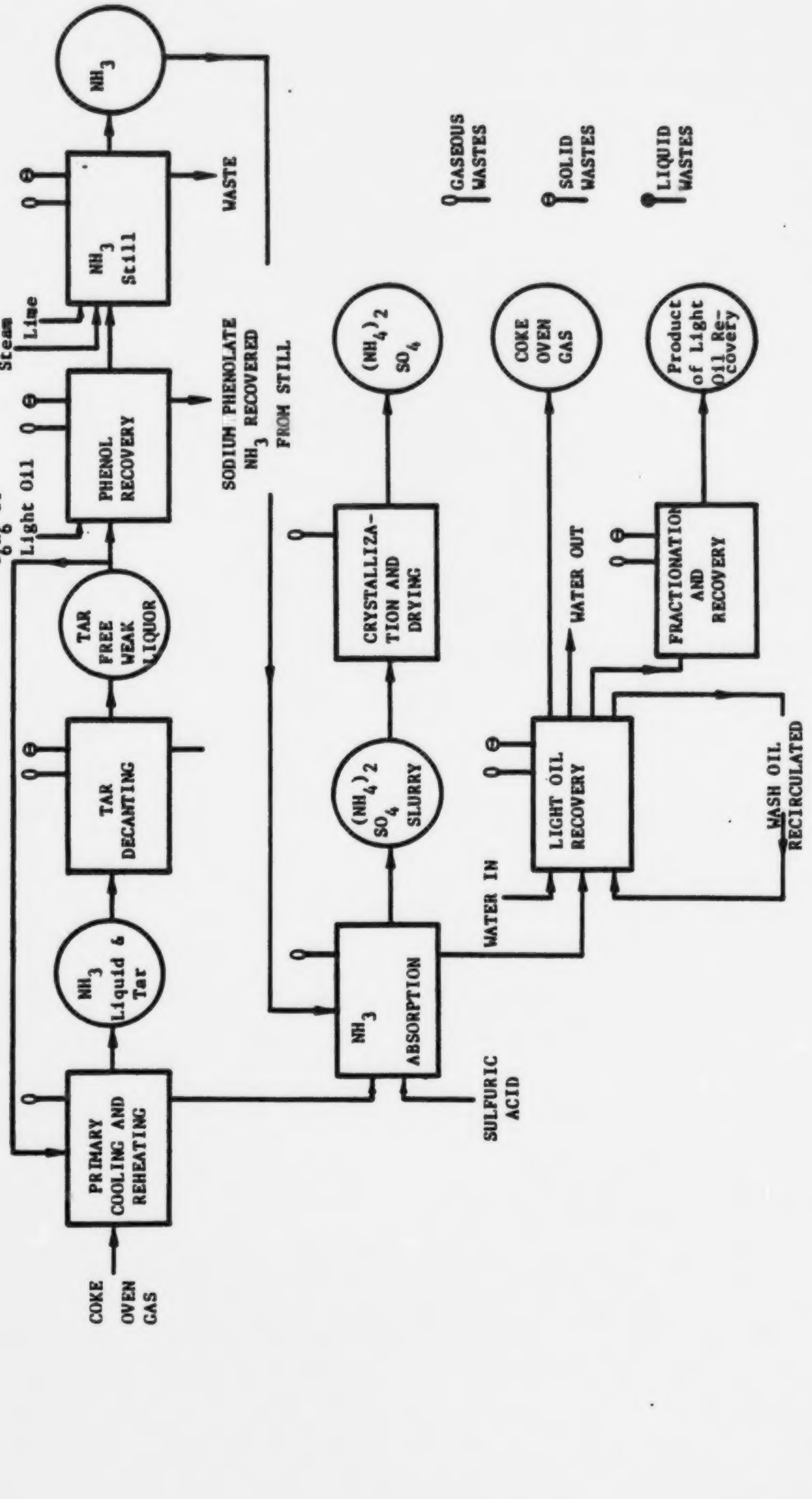
COKE OVEN GAS
PRIMARY COOLING AND REHEATING
NH3 Liquid & Tar
TAR DECANTING
TAR FREE WEAK LIQUOR
C6H6 or Light Oil
PHENOL RECOVERY
Steam
Lime
NH3 Still
WASTE
NH3
SODIUM PHENOLATE
NH3 RECOVERED FROM STILL
SULFURIC ACID
NH3 ABSORPTION
(NH4)2 SO4 SLURRY
CRYSTALLIZATION AND DRYING
(NH4)2 SO4
WATER IN
LIGHT OIL RECOVERY
WATER OUT
COKE OVEN GAS
FRACTIONATION AND RECOVERY
Product of Light Oil Recovery
WASH OIL RECIRCULATED
GASEOUS WASTES
SOLID WASTES
LIQUID WASTES

FIGURE 5.3. Coke By-Products Recovery (U.S. EPA, Feb. 1977).

Ammonia vapors from the primary cooling and heating operations and the ammonia still are absorbed in a dil. H_2SO_4 solution, the $(NH_4)_2SO_4$ product is crystallized from the resulting slurry. Gases leaving the ammonia absorber are scrubbed with recycled wash oil to remove light oil. The light oil is refined to produce benzene, toluene and xylene. The uncondensed "coke oven gases" are sent to a gas holder and contain mainly CO_2, CO, N_2,H_2, O_2 and H_2S. The compositions are given in Table 5.2.

TABLE 5.2. COKE OVEN GASES (AFTER BY-PRODUCT RECOVERY) (Ess, 1948; Wilson, et al. 1980)

Component	Kg/ton of Coal
CO_2	10.42
CO	31.54
H_2	13.66
N_2	3.85
O_2	7.17
H_2S	3.25

It is suggested that H_2S be removed prior to ammonia absorption using the Claus or Stretford process (Dunlap, et al. 1973).

One of the major pollutants from light oil recovery is cyanide (Allen, 1979). HCN contained in the gas leaving the cooling tower at one site amounted to 0.56 lb/ton of coke.

It is suggested that cyanide be removed by adsorption or other suitable methods. About the same amount of cyanide is expected to be in the cooler wastewaters. Biological systems followed by nutrient addition in the form of phosphoric acid have been reported to produce a reduction of cyanide of up to 95% (Hofstein and Kohlmann, 1980).

5.4 IRON MAKING

Blast furnaces are large cylindrical structures in which molten iron is produced by the reduction of the iron bearing ores with coke and limestone. Reduction is promoted by blowing heated air into the lower part of the furnace. As the raw materials melt and decrease in volume, the entire mass of the furnace charge descends. Additional raw materials are added (charged) at the top of the furnace to keep the amount of raw materials within the furnace at a constant level.

Iron oxides react with the hot CO from the burning coke, and the limestone reacts with impurities in the iron ore and coke to form molten slag. These reactions start at the top of the furnace and proceed to completion as the charge passes to the bottom of the furnace. The molten slag, which floats on top of the molten iron, is drawn off (tapped) by way of a "tapping hole." Blast furnace operations within the U.S. produce greater than 99% of the basic iron. The total rated capacity of all U.S. plants is 321,847 tons/day.

The gases which are produced in the furnace are exhausted through the top of the furnace. These gases are cleaned, cooled, and then burned to preheat the incoming air to the furnace. Generally, gas cleaning involves the removal of the larger particulates by a dry dust collector, followed by a variety of wet scrubbers for finer particle removal. Many of the same pollutants found in coke plant wastewaters are also found in iron making wastewaters. The phenolic pollutants found in iron making wastewaters are attributable to the coke used in the iron making process. Cyanide and ammonia (reaction products formed within the furnace or transferred from the coke charge to the furnace gases) are carried over with the gas stream and transferred to scrubbing waters. Table 5.3 lists some of the pollutants in these scrubbing waters (U.S. EPA, Dec. 1980b).

TABLE 5.3. ANALYSIS OF BLAST FURNACE SCRUBBER WASTEWATERS FLOW RATE, GALLON/TON IRON 2057

Pollutant	Concentration mg/1
Ammonia	63.2
Cyanide	16.9
Phenols	2.77
Flouride	23
Suspended Solids	693
pH	7.1 - 8.3

The cleaned gases are then cooled with direct contact sprays in large gas cooling vessels before being burned.

About 90% of the present blast furnace wastewater treatment systems include recycle (after thickening) and discharge only about 5% to 10% of the process flow. The dewatered solids from thickener are either sent to the sintering operations or to off-site disposal. These solids contain Zn, Ag, Ni, Cu, Pb, etc. The effluent concentrations are listed in Table 5.4.

TABLE 5.4. WASTEWATER THICKENER UNDERFLOW (U.S. EPA, DEC. 1980b) FLOW RATE 87 GALLONS/TON IRON

Pollutant	Concentration mg/l
Cu	0.19
Pb	2.11
Ni	0.10
Ag	0.023
Zn	27.5

It is suggested that the gas cleaning system be modified to use few and if possible no wet scrubbers. For fine particle collection the possibility of using electrostatic filters or magnetic filters should be studied. The cleaned gases are generally cooled in spray towers (before being burnt) thus producing more wastewaters. Instead it is suggested that 1) cleaned gases be burnt directly, or 2) be cooled by heat exchange with air feed to the blast furnace and then burnt.

It was suggested for the coke by-product recovery process that organic compounds be removed by adsorption on activated carbon. Similar systems are proposed for removal of organics from the blast furnace wastewaters. The use of biological oxidation and alkaline chlorination systems for treatment of these wastewaters to remove HCN is also suggested.

Hofstein and Kohlman (1979) report that one of the non-U.S. plants they visited uses Caros Acid (per-monosulfuric acid - H_2SO_5) to reduce cyanide and phenol levels in the blast furnace wastewaters to 0.2 mg/l HCN and 0.5 mg/l phenol. The normal influent level of phenol at that plant was 2 mg/l. The addition of polyphosphate in the cooling towers had been reported to aid in CN removal but at CN levels above 10 mg/l it was not effective. Another plant theorized, based on operating experience, that the formation of metallo-cyanide complexes adsorbed in the sludge reduced cyanide levels from 0.2 mg/l to 0.1 mg/l. Another plant in West Germany uses aeration prior to discharge to the clarifiers as an integral part of the gas cleaning water recirculation system. The purpose of aeration is to strip CO and CO_2 from the water and to precipitate $CaCO_3$. A portion of the clarifier sludge is recycled to act as a seed and enhance precipitation and sedimentation.

Osantowski and Gienopolos (1979) obtained pilot plant data on the applicability of advanced waste treatment methods for upgrading blast furnace wastewaters. The treatment methods investigated included: alkaline chlorination, clarification, filtration (dual media and magnetic), ozonation, activated carbon and reverse osmosis. Alkaline chlorination consisted of elevating the pH of the oncoming wastewaters to 11.0-11.5 with addition of sodium hypochlorite for oxidation of cyanide; followed by neutralization for ammonia removal. The settled effluent was dechlorinated by activated carbon. These studies showed that above a $Cl_2:NH_3$ ratio of 7.3:1, NH_3 levels dropped sharply to as low as 0.48 mg/L, NH_3 removal was high and all other oxidizable contaminants were also removed. Further research is needed to optimize the $Cl_2:NH_3$ ratio to obtain the best ammonia removal. Ozonation was determined to be effective in meeting discharge levels. Prefiltered wastewater was elevated to a pH of 10.5 prior to ozonation. The ozone dosage varied from 0-1, 500 mg/l of wastewater treated and contact times from 60-240 minutes. NH_3 and cyanide levels of 3.1 and 0.001 mg/l were achieved. Research is required to find the optimal pH and contact time.

Metals in the raw wastewaters may be better removed by sulfide precipitation. The use of excess sulfide in a treated effluent may cause an objectionable odor problem. A decrease in pH might affect personnel if the wastewater becomes acidic. In view of these objections, a ferrous sulfide slurry may be a good choice since it does not dissociate readily, thus, controlling the pressence of excess sulfide. To this date, there are no furnace wastewater systems currently using sulfide precipitation (U.S. EPA, Dec.1980b), even though this technology has been demonstrated in the metal finishing industry. It is suggested that applicability of sulfide precipitation to remove metals from blast furnace wastewaters be investigated.

There are two types of dust materials collected from the blast furnace operations; 1) dry-collected dusts are obtained from cyclone dust collectors, and , 2) wet-collected dusts are obtained from wet scrubbers after reducing the water content by thickners and filters. The bulk of this material is used as landfill even though some is utilized in the sintering operations. Coke, pellet, and BOF slag fragments are the predominant components of the dry dust materials and include significant quantities of hematite, magnetite, graphite, calcium carbonate, wusite and silica. The size distribution of these dusts ranges from 2.5 mm to 0.014 mm. Wet-collected dusts are similar to dry-collected dusts and average 24% by weight Fe and 45% by weight C, with about 68% of the material less than 60.5 μm in size. The high and variable carbon content of this material makes it difficult to use in the sintering operations. Furthermore, the high amounts of zinc in the wet-collected dusts can impede the blast furnace operations if recycled. A briquetting method for dezincing these dusts has been developed (Allen, 1979). Typical analysis of salable zinc oxide dust is 63.3% Zn, 6.9% Pb, and 1.2% Fe. Another possible alternative dezincing process may be extracting the zinc from collected dusts.

The Waelz process is a direct reduction technique that has been used for 20 years to refine low grade zinc ores. The Berzelium and Lurgi companies conducted a large scale experiment in Dinsburg, Germany that used iron and steel material dusts (Rausch and Serbert, 1948). They observed that dezincification was possible with a continuous process, 95% of the zinc and 50% of the alkalis were removed and 95% of iron was metallized. This process was found to operate more economically on a lower throughput (10^5 tons/year) than other direct reduction processes (U.S. EPA, April 1979) and it is less sophisticated since it does not require pelletizing before reduction.

Advances in technologies such as auxiliary fuel injection, higher hot blast temperatures, moisture injection, and oxygen enrichment have been major factors in increasing the efficiency of the blast furnace process. Based on a statistical analysis technique of certain operating parameters, Quigley and Sayles (1974) concluded that as the coke stability is improved by increasing bulk density and coking time, and improving coal grinding. They also found that an increase of 1.5% in ash content of the coke resulted in over 50% off-quality iron over a two day period. Thus, a study aimed at improving blast furnace performance by improving the coking process is suggested.

Slags from the blast furnace usually come into contact with water immediately after their removal from the blast furnace. The reaction between slag and water produces H_2S and SO_2 among other gases, which even though small in quantity can cause odor problems. Knowledge on the mechanism of H_2S and SO_2 formation is limiting. It is believed that SO_2 results primarily from the oxidation of H_2S. It is desirable to suppress the formation of sulfurous gases, primarily H_2S. In laboratory experiments Kaplan and Rengstroff (1973) showed that treatment of the slag with the oxidizing materials Fe_2O_3, CO_2, $CaCO_3$, open-hearth slag or steam decreased the emission of H_2S. In-plant trials where commercial batches of blast furnace slag was treated with steam prior to water quenching the hot solid slag and molten slag, the steam treatment resulted in an increase in the emission of H_2S.

One important process modification then, would be, to optimize slag quenching methods to decrease H_2S emissions. This would require a better understanding of H_2S and SO_2 formation during slag quenching and the effect of various additives.

Another option is to produce elemental sulfur from H_2S by the Claus or Stretford Process. If HCN is found to cause fouling of the Claus catalyst beds or decrease the life of Stretford absorption solution, HCN may have to be removed from the feed gases by the polysulfide process which is known to have removal efficiences of up to 90% of HCN (Hill, 1945).

Cyanides are thought to form in the blast furnace according to the following reaction:

$$K_2O + 3C + N_2 \rightleftarrows 2KCN + CO \qquad (5.1)$$

This reaction is favored at high temperatures and in the absence of CO. The oxidation of cyanides takes place according to the following reaction:

$$2KCN + 4CO_2 \rightleftarrows K_2CO_3 + N_2 + 5CO \qquad (5.2)$$

It would appear that conditions favorable for the formation of cyanides, i.e., the coexistence of coke, alkali oxides, and N_2 at high temperatures and in a reducing atmosphere are inherent in the operation of the iron blast furnace. In contrast, it may be possible, at least in principle, to modify the conditions in the stack region, so that oxidation of cyanides is promoted. Very little work has been done, however, on the kinetics of the reactions in the formation and oxidation of cyanides in the blast furnace. Sohn and Szekely (1943) assumed mass transfer to the KCN particle to be rate controlling and concluded that there may be a real possibility of reducing the net emission of cyanides from the blast furnace by the appropriate manipulation of the temperature and CO/CO_2 profiles within the stack. It is suggested that research efforts be directed at obtaining kinetic information on the formation and oxidation of cyanides in the blast furnace and at optimizing stack design and operation to reduce the total cyanide in the effluent gases.

5.5 STEEL MAKING

Steel is an alloy of iron containing less than 1.0% carbon. Steel making is basically a process in which carbon, silicon, phosphorous, manganese, and other impurities present in the raw hot metal or steel scrap, are oxidized to specific minimum levels. The hot steel is then either teemed into ingots or transferred to a continuous casting or pressure casting operation for direct conversion into a semi-finished product.

The basic raw materials for the steel making processes are hot metal or pig iron, steel scrap, limestone, burned lime, dolomite, fluorspar, iron ores and iron bearing minerals such as pellets, mill scale and waste solids from the furnaces. Various types of steel are manufactured by adding alloying agents either to the hot charge in the furnace or to the ladle of steel after the hot steel is "tapped" from the furnace. The three types of steel making processes are:

1. Basic Oxygen Furnace (BOF)

2. Open Hearth Furnace (OH)
3. Electric Arc Furnace (EAF).

A comprehensive discussion of the various operations that constitute each of these processes is given by McGannon (1964).

The large quantities of airborne gases, dusts, smoke, and iron oxide fumes generated in the steel making processes are collected and contained by various gas cleaning systems. Depending on the type of gas cleaning system used, wastewaters discharges or sludge generation can result. The basic gas treatment systems used are:

BOF	Semi-wet
	Wet-Suppressed Combustion
	Wet-Open Combustion
	Semi-wet
OH	Wet
EAF	Semi-wet
	Wet

The semi-wet air pollution control systems use water to partially cool and condition the waste gases and fumes prior to final particulate removal in dry collectors such as precipitators or baghouses. Wet air pollution control systems use water not only to cool the waste gases but also to scrub the fume particles from the waste gases. BOF uses combustion systems, suppressed or open, to control CO emissions.

The two variations of the BOF process are the Kaldo process and the Q-BOP furnace. At present, there is only one Kaldo installation and only three Q-BOF installations in the United States. The waste products from the BOF steel making process include airborne fluxes, slag, carbon monoxide and dioxide, and oxides of iron (FeO, Fe_2O_3, Fe_3O_4) emitted as submicron dust. Also, when hot metal (iron) is poured into ladles or the furnace, submicron iron oxide fumes are released and some of the carbon in the iron is precipitated as graphite, commonly called "kish". Approximately 1% to 2% of the ingot steel is ejected as dust. The primary gas constituent emitted from the BOF during the oxygen blowing cycle is CO. CO will burn outside of the BOF, if allowed to come in contact with outside air (open combustion). If outside air is prevented from coming in contact with the CO gas, combustion is retarded (suppressed combustion).

In the Open Hearth (OH) process, steel is produced in a shallow rectangular refractory basin, or hearth, enclosed by refractory lined walls and roof. OH furnaces can use all scrap steel charge; however, a 50% scrap/50% hot metal charge is typical. Fuel oil, coke oven gas, natural gas etc. are burned as fuel and the hot gases are circulated above the raw material charge. The waste gases are water cooled, scrubbed with recycled water and sent through a electrostatic precipitator before being vented. The waste products resulting from the OH process are slag, iron oxides as submicron dust, waste gases (consisting of air, CO_2 and water vapor), SO_x and NO_x (due to the nature of certain fuels being burned) and oxides of zinc.

The Electric Arc Furnace (EAF) steel making process produces high quality alloy steels in refractory lined cylindrical furnaces using a cold steel scrap charge and fluxes. The waste products from EAF process are smoke, slag, CO, CO_2, metal oxides (mainly iron) emitted as submicron particles and zinc oxides.

Raw wastewater characteristics are given in Table 5.5 (U.S. EPA, Dec. 1980b).

TABLE 5.5. RAW WASTEWATERS FROM STEEL MAKING OPERATIONS CONCENTRATION (mg/l)

I. Basic Oxygen Furnace	
a. Semi-wet (Flowrate = 429 gal/ton)	
Suspended Solids	345.0
Cu	0.004
Pb	1.5
Zn	1.0
b. Wet-Suppressed Combustion (Flowrate = 982 gal/ton	
Suspended Solids	1500.0
Cr	0.5
Cu	0.25
Pb	15.0
Ni	0.5
Zn	5.0

TABLE 5.5. Continued

c. Wet-Open Combustion (Flowrate = 446 gal/ton)	
Suspended Solids	4200.0
Cd	0.5
Cr	5.0
Pb	1.0
Zn	5.0
II. Open Hearth Furnace	
a. Semi-Wet (Flowrate = 1163 gal/ton)	
Suspended Solids	500.0
Cr	0.8
Cu	0.8
Cyanide	0.04
Zn	0.5
b. Wet (Flowrate = 554 gal/ton)	
Suspended Solids	1100.0
Cu	2.0
Pb	0.6
Zn	200.0
III. Electric Arc Furnace	
a. Semi-Wet (Flowrate = 60.4 gal/ton)	
Suspended Solids	2200.0
Cu	2.0
Pb	30.0
Zn	125.0

TABLE 5.5. Continued

III. Electric Arc Furnace Cont'd	
b. Wet (Flowrate = 3060 gal/ton	
Suspended Solids	3400.0
Arsenic	2.0
Cd	4.0
Cr	5.0
Cu	2.0
Pb	30.0
Zn	125.0

The treatment methods presently used do not attempt to remove these toxic metals exclusively (U.S. EPA, Dec. 1980b). Sulfide precipitation to enhance the precipitation of metals from wastewaters before recycle is a suggested pollution control approach. There is a need to develop extraction and ion exchange systems to remove toxic metals formed in the steel furnace wastewaters.

Suspended solids in steel making wastewaters are very fine, red in color, and are principally iron oxide. Magnetic separation can decrease the level of suspended solids to 25-30 mg/l (Centi, 1973).

5.6 ACID PICKLING

Acid pickling is the steel finishing process in which steel products are immersed in heated acid solutions to remove surface scale. Based on the type of pickling acid used, this process can be subdivided into:

1. Sulfuric Acid Pickling
2. Hydrochloric Acid Pickling
3. Combination Acid Pickling

Wastewaters are generated by three sources in the pickling process. The largest source is the rinsewater used to clean the acid solution from the product after it has been immersed in the pickling solution. The second source is the spent pickling acid liquor which is used to treat the steel product. The spent pickle liquor is a small volume waste, containing high concentrations of iron and toxic metal pollutants. Wastewater from the wet acid fume scrubbers is the third source.

Rinse water discharge flows can be minimized with a cascade of countercurrent rinse systems. These systems reduce water flow, concentrate the pollutants in the last rinsing chamber, and achieve more thorough rinsing (U.S. EPA, Dec. 1980c).

The most common method of recovering spent sulfuric acid is acid recovery by removing ferrous sulfate through crystallization and rinsing the concentrated acid (U.S. EPA, Dec. 1980c).

The spent liquor from hydrochloric acid pickling contains free hydrochloric acid, ferrous chloride, and water. This liquor is heated to 1,050°C, at this temperature the water is completely evaporated and $FeCl_2$ decomposes completely into Fe_2O_3 and HCl gas. The iron oxide is separated and removed and HCl gas is reabsorbed in the water.

Recycle systems, with recycle rates as high as 90%-95% of the total wastewater flow are used to control pollutants generated during the scrubbing of acid fumes. Recycle rates are limited by the build-up of solids. Lime and sulfide precipitation are suggested to improve precipitation of metals in the wastewaters.

Temperature and agitation are important operating factors in the pickling process. The temperature of pickling dramatically effects the reaction rate. Agitation is probably the most ignored aid to good pickling. The speed of pickling can be increased significantly by properly agitating the acid bath or using the steel product during the pickling operation. One method of agitation is an air-operated, mechanical agitation system. An added benefit of this system is that the evaporation caused by air agitation concentrates, rather than dilutes, the acid bath. It is suggested that process improvements be aimed at decreasing pickling time and maintaining good agitation and high enough acid concentration levels during pickling.

Table 5.6 lists the various process modifications suggested for control of pollution from the iron and steel industry.

5.7 RECOMMENDED AREAS FOR PROCESS MODIFICATIONS RESEARCH

After careful evaluation of the available literature, the following areas are recommended for further research:

- Use of refined or cleaned coal in coke making
- Study of the formation of cyanides and carbonyls during coking in order to prevent or reduce pollutant formation.
- Dry coke quenching of U.S. Coals to eliminate quench water contamination.
- The effect of process variables such as coal grinding and coking time on coke produced. This would be used to improve the quality of coke stability in order to enhance blast furnace performance.
- Development of biological oxidation systems to remove HCN from by-product coke making wastewaters.
- Absorption of H_2S from coke oven gases by Claus or Stretford process.
- Development of better CN removal systems from blast furnace wastewaters by using additives such as Caros acid (H_2SO_5) and polyphosphate, and by aeration.

Table 5-6. Pollutants and Suggested Control Strategy Iron and Steel Industry

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Coke Making	Organometallics, Carbonyls, HCN, SO_x, H_2S	Emissions from coke ovens	Toxic gases	Use of refined coal, better control of coking operations.
	Phenols, Sulfates, Chlorides, Ammonia, Cyanides	Wastewaters from coke quenching	Dissolved and suspended solids	Conversion to dry coke quenching with particulate removal
Coke By-Product Recovery	H_2S	Coke oven gases having by-product recovery	-------	Removal of H_2S by Claus or Stretford Process
	HCN	Cooler Wastewaters	---------	Removal of HCN by biological oxidation systems
Iron Making	Metals (Zn, Pb, etc.)	Blast Furnace wastewaters	Suspended solids	Conversion from wet to dry gas cleaning systems - electrostatic, magnetic filters

Table 5-6. Pollutants and Suggested Control Strategy for Iron and Steel Industry (Cont'd)

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Iron Making	Cyanide	Blast Furnace Wastewaters	---------	Optimization of pH and contact time to improve alkaline chlorination, use of additives such as H_2SO_5 and polyphosphates
	Zinc	Blast Furnace Dusts	---------	Solvent extraction of Zn or removal by Walez process, recycle treated dusts to sintering plant
	H_2S, SO_2	Blast Furnace slag Quenching	Inorganic gases	use of additives to improve oxidation of H_2S
	Cyanides	Blast Furnace	Inorganic particulates	Improved stack design and operation to optimize oxidation of cyanides

Table 5-6. Pollutants and Suggested Control Strategy for Iron and Steel Industry (Cont'd)

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Steel making	Zn, Cr, Pb, Cu, iron oxide	Wastewaters from cooling and conditioning of gases from steel making furnaces	Suspended, dissolved solids	Sulfide precipitation of toxic metals & recycle of treated wastewaters magnetic separation of suspended iron oxides, solvent extraction of metals
Acid Pickling	Spent Pickle Liquor (SPL)	---------	Inorganic acids, suspended toxic metals, iron	Improved pickling process by temperature control and good agitation to decrease SPL, recovery of acid
	Rinse Waters	Cleaning of treated product after pickling	Inorganic acids, suspended toxic metals, iron	Minimizing rinsewater discharges by using cascade or counter-current rinse systems

- Optimization of pH and contact time to improve alkaline chlorination and ozonation to upgrade blast furnace wastewaters.
- Solvent extraction of Zinc or dezincification by Walez process to remove zinc from blast furnace dusts. Such zinc removal can facilitate the use of treated dusts in the sintering process.
- Study of kinetics of H_2S and SO_2 formation during blast furnace slag quenching to develop methods by which H_2S formation can be decreased.
- Study the kinetics of formation and oxidation of cyanides in the blast furnace to optimize the design and operation of the stack in order to oxidize the cyanide.
- Development of solvent extraction and sulfide precipitation methods to remove toxic metals from the recycled steel plant wastewaters.
- Study the effect of temperature and agitation in order to optimize pickling operations.

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CHAPTER 6

PAPER AND PULP INDUSTRY

6.1 INTRODUCTION

The pulping process, kraft (or sulfate) pulping in particular, is discussed in this chapter. Pulping wood is the initial process in the manufacture of paper and paper products. The pulping process is the conversion of fibrous raw material, wood, into a material suitable for use in paper, paperboard, and building materials. Pulp is the fibrous material ready to be made into paper.

There are four major chemical pulping techniques: (1) kraft or sulfate, (2) sulfite, (3) semichemical, and (4) soda. Of the major pulping techniques, the kraft or sulfate process produces over 80% of the chemical pulp produced annually in the United States. In 1970, there were 116 mills producing 29.6 million tons of pulp by the kraft process. During the same year the pulp and paper board consumption was 56.8 million tons (U.S. EPA, Sept. 1973).

6.2 KRAFT PULPING

The two basic components of the pulp wood are cellulose and lignin. The cellulose fibers, which constitute the pulp, are bound together by lignin, thus, any process manufacturing pulp must remove the lignin. The Kraft process employs chemical dissolution of the lignin. The flow chart of the kraft process is depicted in Figure 6.1.

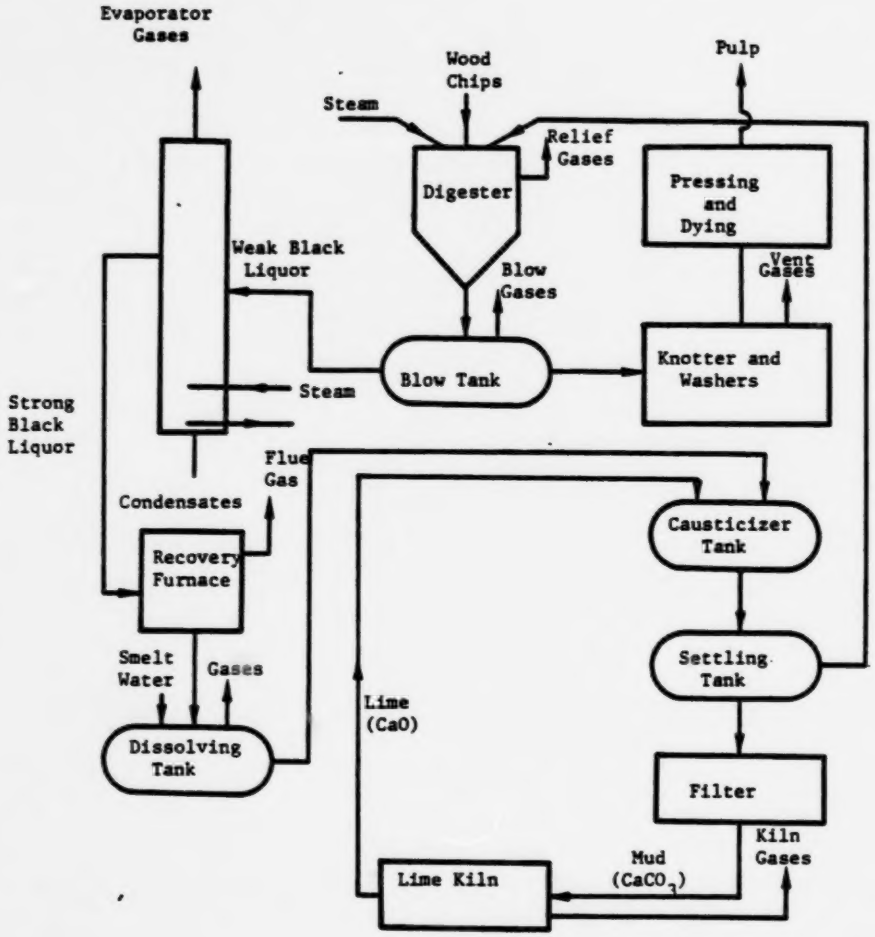
Evaporator Gases
Wood Chips
Pulp
Steam
Relief Gases
Digester
Pressing and Dying
Weak Black Liquor
Blow Gases
Vent Gases
Strong Black Liquor
Steam
Blow Tank
Knotter and Washers
Flue Gas
Condensates
Causticizer Tank
Recovery Furnace
Settling Tank
Smelt Water
Gases
Lime (CaO)
Dissolving Tank
Filter
Kiln Gases
Mud (CaCO3)
Lime Kiln

Figure 6.1. Flow Chart of Kraft Pulping Process (U.S. EPA, Sept. 1973).

The typical pollutants from the kraft pulping process are hydrogen sulfate, methyl mercaptant, dimethyl sulfate, and dimethyl disulfide. The pollutants containing sulfur are collectively called total reduced sulfur (TRS). Hydrogen sulfite emissions are a direct result of sodium sulfide breakdown in the kraft cooking liquor. Methyl mercaptant and dimethyl sulfide are formed in the reactions with lignin. Dimethyl sulfide is formed thorugh the oxidation of mercaptant groups derived from the thiolignin.

The kraft process as a whole can be subcategorized into two parts; actual pulping, and recovery. The pulping occurs in the digester system followed by the pulp wash. The recovery refers to multiple effect evaporators (MEE), recovery furnace, smelt dissolver, and lime kiln, all of which serve to recover the white liquor and heat.

6.2.1 Digester System

There are two types of digesters, continuous and batch digesters. The composition and quality of digester gases will differ between the two digester types. Batch digesters often present air pollution problems because of gas surges produced during blowing. Continuous digesters, however, present much smaller pollution problems than batch digesters because contaminated condensates and odorous gases flow at a regular rate. Most of the kraft pulping is currently done in batch digesters (Goodwin, 1978). The following discussion entails only the batch digester system.

The digestion process is a delignification process in which white liquor and wood chips are heated to 170-175°C. White liquor is composed of sodium sulfide (Na_2S) and sodium hydroxide ($NaOH$).

Emissions from the digester are caused by two streams; the relief gases and blow gases. The relief gases are the ventilation gases which maintain the digester at the proper pressures (100-135 psig). The blow gases, steam and other gases, are from the blow tank where the cooking liquor is drained from the pulp. Both the relief and blow gases are condensed for heat recovery. Table 6.1 gives the pollutant emission rates for the digester system.

TABLE 6.1. TYPICAL EMISSION RATES FROM BATCH DIGESTER IN kg SULFUR/TON OF ADP* (U.S. EPA, JAN. 1978)

Pollutant	Blow Gases	Relief Gases
H_2S	0-0.1	0-0.5
CH_3SH	0-1.0	0-0.3
CH_3SCH_3	0-0.25	0.05-0.8
CH_3SSCH_3	0-0.1	0.05-1.0

* ADP - Air Dried Pulp

Mercaptants and methyl sulfide are unavoidable by-products of kraft pulping, however, there are few measures which can limit their production. Generally, high temperatures, high sulfidity and long reaction times favor the production of the sulfur compounds (Douglas, 1966). Thus, if the sulfidity of the white liquor is kept at a minimum, the formation of gaseous sulfur compounds will be reduced. Sarkanen, _et_ _al_. (1970), suggests a 20% sulfidity for most paper mills.

Final emissions of the digester system is determined by the effective operation of the condenser (heat exchanger) units. Experience shows that the surface area of the heat exchanger, thought originally to be sufficient may later prove to be too small (U.S. EPA, Oct. 1976). This is due to fiber carryover by the blow gases and consequent fouling of the heat transfer surfaces. The fiber carryover is caused by excessive gas velocities at the entrance of the flow exhaust pipe. The minimum velocity to suspend solid particles is 18 fps, and the actual velocity in the blow tank reached 46 fps (Martin, 1969). The recommendations to reduce fiber carryover are: decrease the digester wood to liquor ratio, relieve the digester to a lower pressure before blowing and/or blowing for a longer time period, installation of a cyclone separator, and initially providing more heat exchange surface.

6.2.2 Brown Stock Washer System

The washing process is a minor source of air pollution as compared to digestion, evaporation, and combustion. The emission of air contaminated with organic sulfur compounds is due primarily to the contact of air with black liquor. The amount of air and sulfur compounds ventilation depends mainly on the type of washing process and equipment. The two main washing processes are displacement and diffusion washing (U.S. EPA, Oct. 1976).

Categorically, displacement washers include vacuum washers and pressure washers. Of the two, the pressure washers' hood vent and foam tank vent will have smaller flow rates and total reduced sulfur (TRS) emissions.

Typical emission rates from the vacuum washers' hood vent and the foam tank are shown in Table 6.2.

TABLE 6.2. EMISSION RATES FROM VACUUM WASHER IN kg SULFUR/Ton ADP (U.S. EPA, October 1976)

Pollutant	Washer Hood Vent	Washer Foam Tank
H_2S	0-0.1	0-0.01
CH_3SH	0.05-1.0	0-0.01
CH_3SCH_3	0.05-0.5	0-0.05
CH_3SSCH_3	0.05-0.4	0-0.03

Diffusion washing is superior to displacement washing, since the washing takes place in a closed reactor. In diffusion washing, ideally, there is no air involved, thus, black liquor oxidation and odor release are very small compared to displacement washing.

Some mills employ contaminated condensates for washing. A study of 17 washing systems indicated an emission rate of 0.014 lb/ton ADP as H_2S using H_2O, and 0.35 lb/ton ADP treating with condensate (U.S. EPA, Sept. 1973). In view of pollution abatement, water is a better washing medium than the condensates. Another possibility is to reduce sulfur contents of the condensate by stripping.

6.2.3 Multiple Effect Evaporator System

Multiple effect evaporators (MEE) are utilized to concentrate weak black liquor from 12-18% solids to 40-55% solids (Goodwin, 1978). The weak black liquor is a mixture of digester spent cooking liquor and stock washer discharge. Basically each effect consists of a heating element and a vapor head. The hot vapors from the vapor heat of a previous effect pass to the heating element of the following effect. The vacuum is maintained by means of rapid condensation of the vapor from the final effect.

This section includes only the most important indirect steam evaporation system from the view point of pollution. Thus, the following discussion is for Vacuum MEE. However, the pollution control strategies can be readily applied to other evaporation techniques. Typical emission rates for MEE are shown in Table 6.3.

TABLE 6.3. EMISSION RATES FROM MEE IN kg SULFUR/TON ADP (U.S. EPA, OCT. 1973).

Pollutant	Emission Rate kg Sulfur/ton ADP
H_2S	0.05-1.5
CH_3SH	0.05-0.8
CH_3SCH_3	0.05-1.0
CH_3SSCH_3	0.05-1.0

The most effective method of reduction of pollution in MEE is to steam strip the condensate and to incinerate the so called noncondensable gases (H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3). Matteson, et al. (1967) successfully stripped the condensate generating overhead vapor of more than 95% hydrogen sulfide, mercaptants, and dimethyl disulfide. Steam stripping was performed in a conventional bubble cap tray stripper resulting in a bottom product of nearly pure and reusable water. The stripped gases and other gases from the MEE can be incinerated in the lime kiln (Walther and Amberg, 1970).

The liberation of H_2S and to a lesser extent CH_3SH depends on the pH of the black liquor. This is due to the acidic nature of both gases. Furthermore, these gases dissociate more readily in an aqueous solution of higher pH. Addition of caustic soda to the weak black liquor can be beneficial in alleviating H_2S and CH_3SH.

The emissions of H_2S and CH_3SH are dependent on the sulfide concentration of the weak black liquor. Oxidation of this weak black liquor can convert sulfide to thiosulfate and CH_3SH to CH_3SSCH_3. These conversions will facilitate the reduction of H_2S and CH_3SH emission from MEE. The condensate from the MEE processing of oxidize weak black liquor will require little, if any, treatment for odor abatement (EPA, 1976).

Furthermore, Galeno and Amsolen (1970) observed several benefits of weak black liquor oxidation with O_2 as compared to lack of oxidation. The oxidation uitlizing O_2 resulted in lower emisisons of H_2S from the MEE, and improved the evaporator condensate water quality.

There are two major factors which should be considered in the effectiveness of weak black liquor oxidation to prevent TRS emission. First, a high degree of oxidation is required. Second, oxidized sulfur compounds have tendencies to revert to sulfide during MEE as well as during extended storage. Long storage periods after black liquor oxidation should be avoided.

6.3 RECOVERY FURNACE SYSTEM

The recovery furnace functions include: (1) recovery of sodium and sulfur, (2) production of steam and, (3) disposition of unwanted components of the dissolved wood. The recovery furnace system generally includes the following units: recovery furnace, flue gas direct contact evaporator, primary particulate control device, and secondary particulate control device. In some cases the direct contact evaporators have been used to contain the particulate emissions or eliminated all together (U.S. EPA, March 1970). Table 6.4 is a listing of emission rates from the recovery furnace.

TABLE 6.4. EMISSION RATES FROM RECOVERY FURNACE (U.S. EPA, OCT. 1976).

Pollutants	Emission Rate kg/ton ADP
H_2S	0-25
CH_3SH	0-2
CH_3SCH_3	0-1
CH_3SSCH_3	0-0.3
SO_2	0-40
SO_3	0-4
NO_x	0.7-5

The particulate emission rates are listed in Table 6.5.

TABLE 6.5. PARTICULATE EMISSION RATES FROM THE RECOVERY FURNACE (U.S. EPA, OCT. 1976)

Emission Source	Emission Rage kg/ton ADP
Recovery System after Electrostatic Precipitator	0.5-12
After Venturi Evaporator	14-50
Flue Gas Dust Load	40-75

The three direct evaporators used in the kraft pulping mills are cascade evaporators, cyclone evaporators, and the venturi recovery unit. The difference between a venturi and the other two evaporators is its efficiency in removing particulates. While cyclone and cascade evaporators remove only 40-50% of the particulate matter, the venturi recovery units can be designed to capture better than 90% of the particulates (U.S. EPA, Sept. 1973). The direct contact evaporator serves as an adsorption unit for SO_2 and nearly all SO_3. Furthermore, it absorbes H_2S emitted from the recovery furnace under conditions of high black liquor pH and low sodium sulfide concentrations in the strong black liquor.

The direct evaporation unit is also a potential source of TRS. However, the emission of TRS depends heavily on the residual sulfide in the black liquor from MEE. For this purpose, some mills employ strong black liquor oxidation. A survey of 32 recovery furnace systems where black liquor oxidation is not used showed sulfur emission ranging from 0.75-31g/Kg ADP, with an average of 7.7g/Kg ADP. Conversely, a survey of 17 units that utilized black liquor oxidation indicated emission ranges of 0.113g/Kg ADP, with an average of 3.7g/Kg ADP (Goodwin, 1978).

It is possible to eliminate the direct contact evaporator in favor of a non-contact design. This change will cause an increase in particulate emissions which would then require installation of a more efficient particulate control device.

The emission of sulfur compounds from the recovery furnace is also dependent on the design of the furnace. The recovery furnace has two functions; recovery of the chemicals in their reduced state (i.e. sulfur should be present as sulfide and not sulfate), and recovery of heat to generate steam for the processes.

Combustion within the recovery furnace is separated into two zones. The first zone must be maintained under reducing conditions, less than the required stoichiometric amounts of air. The products of this zone discharge chemicals in the molten state with the sulfur present mainly as sulfide and organic matter as a gas having considerable heat value. The second zone of combustion starts with the addition of secondary air. The secondary air should be supplied in 10-20% excess of the amount required for complete combustion.

The release of sodium from the burning char of black liquor depends on the temperature and the gas conditions in the border zone between the bed and the flue gas. The TRS release to the flue gas is affected by the total sulfur concentration and the sodium to sulfur ratio. Since the sodium/sulfur ratio in the smelt bed depends on temperature, the release of sulfur to the flue gas is also a function of temperature. Hydrogen sulfide may be present in the flue gas in the primary air combustion zone at 50-100ppm if the zone between the bed and the flue gas are kept at the optimal temperature. Hydrogen sulfide concentrations of 15,000 ppm have been observed in this region when black out conditions are present (black out conditions refers to insufficient rate of combustion in the hearth). Typically, a low temperature favors the presence of S and H_2S (U.S. EPA, Oct. 1976).

There are several advantages in raising the primary air temperature. The velocity for the same flow of air will increase and improve the sodium evaporation from the bed. Also, the release of sulfur from the bed decreases.

Immediately after introduction of secondary air, the final combustion starts. The amount of primary air for most furnaces must be more than 110% and less than 125% of the theoretical air to avoid formation of stick dust. Stick dust has a tendency to foul the heating surfaces. The secondary air should be supplied to the furnace such that it mixes with the gas coming from the primary air combustion zone. Therefore, efficient regulation and method of introduction of secondary air is important in the generation of stick dust.

The variable effecting the TRS emissions from the recovery furnace are as follows: quantity and method of introduction of combusted air, the rate of black liquor feed, the degree of turbulance in the oxidation zone, the O_2 content of flow gas, the spray pattern and droplet size of the liquor fed to the furnace, and the degree of disturbance in the smelt bed. These variables are independent of the presence or absence of a direct contact evaporator (Theon, et al. 1968).

Teller and Amberg (1975) have developed a control technique for use in the recovery furnace which utilizes alkaline adsorption with carbon activated oxidation of the scrubbing solution. Pilot plant studies showed this technique is capable of reducing TRS emissions from 20-1500 ppm to 1 to 10 ppm. This method would also alleviate particulate and SO_2 emissions (Teller and Amberg, 1975). Another effective adsorption method is the TRS system potential by the Weyerhaeuser Company. The TRS scrubber adsorbs up to 99% of H_2S and collects about 85% of the particulate matter.

Nitrogen oxides are generated in the recovery furnace at a rate of 0.7-5 kg/ton ADP (U.S. EPA, Oct. 1976). The reduction of NO_x production lies in provisions for facilitation of a heat sink in the recovery furnace. The endothermic reaction of Na_2SO_4 to Na_2S in the smelt bed also acts as a heat sink to inhibit excessive flame temperatures. A reducing atmosphere above the smelt bed will also reduce NO_x formation. The supply of air can be arranged to spread out the flame front, and in that way, inhibit the increase in gas temperature.

6.3.1 Smelt Dissolving Tank

The molten smelt accumulated in the recovery furnace, as a result of combustion, is dissolved in water in the smelt dissolving tank. Dissolution of the molten smelt (sodium carbonate and sodium sulfide) in water forms a green liquor. The dissolution is aided by agitators and steam, or a liquid shatterjet system, to break up the smelt stream before it enters the solution. The large volume of steam generated by the contact of smelt with water is vented. Table 6.6 depicts the emission rates from the smelt dissolving tank.

TABLE 6.6. EMISSION RATES FROM SMELT DISSOLVE TANK (U.S. EPA, OCT. 1976)

Pollutants	Kg Sulfur/ton ADP
H_2S	0-1.0
CH_3SH	0-0.8
CH_3SCH_3	0-0.5
CH_3SSCH_3	0-0.3
	Kg/ton ADP
Particulate Emission (After Control Device)	0.01-0.5
SO_2	0-0.2

Particulate matter contains dissolved and undissolved NaOH, Na_2CO_3, and Na_2S. The particulate emissions are captured from escaping vent gases by mist eliminator pads. Typical efficiency of the pads for particulate removal is 70-90%, however, higher efficiencies can be achieved by facilitating the smelt tank with a spray or packed scrubber in addition to mist eliminator pads. Combinations of this type can be 98% efficient in removing particulate matter (U.S. EPA, Oct. 1976). Another alternative is to combine vent gases from the smelt tank with flue gases from the recovery furnace prior to entering the particulate collection device. However, the effectiveness of a electrostatic precipitator is reduced due to the water vapor content of the smelt tank vent gases. Furthermore, the Na_2S entrained in the smelt tank vent gases coming into contact with CO_2 from the recovery furnace may promote formation of H_2S. It is evident that the best particulate control device for the smelt tank is a combination of mist eliminator pads and a scrubber.

The TRS emissions depend on the sulfide content of particulate matter, the turbulance in the dissolving tank, the type of solution used in a scrubber, if present, and pH of the scrubber liquor. Fresh water is the best solution for scrubbing and is capable of producing 0.001 lb sulfur/ton ADP (Martin, 1969).

6.4 LIME KILN

The green liquor is converted to white liquor in the lime kiln. This unit is an essential element of the closed-loop system. The kiln calcines the calcium carbonate which precipitate from the causticizer to produce quicklime (CaO). The calcined calcium carbonate precipitate is also called lime mud. The quicklime is wetted (slacked) by the water in the green liquor solution to form calcium hydroxide for the causticizing reaction.

The mud is contacted by the hot gases produced by the combustion of natural gas or fuel oil and proceeds through the kiln in the opposite direction of the gas flow. The lime mud is a 55-60% solid-water slurry and is fed at elevation to the kiln. In the upper part of the kiln the mud dries while at the lower end, the high temperature zone (1800-2000°F), it agglomorates into small pellets and is calcined to CaO. Typical emission rates from lime kiln are given in Table 6.7.

TABLE 6.7. LIME KILN EMISSION RATES (U.S. EPA, OCT. 1976)

Pollutants	Lime Kiln Exhaust & kg Sulfur/ton ADP	Lime Slaker Vent kg Sulfur/ton ADP
H_2S	0-0.5	0-0.01
CH_3SH	0-0.2	0-0.01
CH_3SCH	0-0.1	0-0.01
CH_3SSCH_3	0-0.05	0-0.01
	kg/ton ADP	kg/ton ADP
SO_2	0-1.4	--
NO_x	10-25	--

Variables affecting the TRS emission of the lime kiln are the temperature at the cold end of the kiln, the O_2 content of the gases leaving the kiln, the sulfide content of the lime mud, and the pH and sulfide content of the water used in the particulate scrubber (NCASI, 1971). If contaminated condensate is used as the scrubbing solution, the exhaust gases could strip out the dissolved TRS and increase the TRS emission from the lime kiln.

The two most important preventive measures in view of TRS emission are; maintenance of the proper process conditions, and scrubbing the exhaust gases with caustic solution. For example, TRS emission can be reduced by a sufficient supply of O_2 and a reduction in sulfide content of the mud.

The lime kiln is operated with excess air and high temperature, both conditions favor the production of NO_x, therefore, any measure to reduce TRS may promote generation of NO_x. Thus, oxides of nitrogen are unavoidable by-products of the lime kiln and any measure to control their release should occur after the kiln.

Table 6.8 summarizes some of the pollution problems associated with the kraft pulping process and suggests control alternatives.

6.5 RECOMMENDED AREAS FOR PROCESS MODIFICATION RESEARCH

After evaluating the available literature, the following areas are recommended for further research by the study:

- Research on digestion of wood chips to determine optimal sulfidity, pH, and temperature to reduce pollution.
- Studies on control of fiber carryover from the blow tank by cyclone and/or by reduction of relief pressure and selection of wood to liquor ratio to prevent TRS emission.
- Comparative studies on design and application of diffusion and displacement washers to minimize TRS.
- Effect of black liquor oxidation and pH control on weak and strong black liquor to reduce TRS emission.

Table 6-8. Pollutants and Control Options in Kraft Pulping Process

Process	Pollutants	Sources in Process	Nature of Pollutants	Pollutant Control Strategy
Digester	TRS, relief & blow gases	Digester Tank blow tank	Organic, gases	Lower sulfidity, lower blow pressure, reduce fiber carryover by cyclone or other methods.
Brown Stock Washer	TRS, noncondensables	Vacuum washer	Organic, gases	Use water as washing fluid, employ diffusion washers.
Multiple Effect Evaporators	TRS, noncondensables	Evaporators	Organic, gases	Treatment of week black liquor by oxidation and with caustic soda. Effective stripping of condensate from the condenser unit.
Recovery Furnace System	TRS, SO_2 SO_3, NO_x Particulates	Recovery furnace direct contact evaporator	Organic and inorganic gases and solids	Strong black liquor oxidation. Use direct contact evaporator, venturi type. Improve design. Alkaline adsorption with carbon-activated oxidation of the scrubbing solution.
Smelt Dissolve Tank	TRS, SO_2, Particulates	Smelt Tank	Organic and inorganic gases and solids	Combination of mist eliminator pad and scrubber unit. Use fresh water for scrubbing.
Lime Kiln	TRS, SO_2, NO_x	Kiln	Organic and inorganic gases	Maintain proper process conditions. Sufficient supply of O_2 and reduction in sulfur content of the mud.

- Studies on the direct and non-contact evaporation in the recovery furnace system to determine capability and merits of each unit in reducing the TRS emission.
- Research on combustion of strong black liquor to prevent black out conditions and stick dust formation by optimizing the design and operating conditions in the recovery furnace.
- Research and application of scrubbing techniques to reduce TRS emission.

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CHAPTER 7

THE PRIMARY ALUMINIUM INDUSTRY

7.1 INTRODUCTION

The primary aluminium industry consists of processing bauxite ore to produce alumina (and occasionally aluminium hydroxide) and processing the alumina to produce aluminium. Approximately, 7.6 x 10^6 tons of alumina were produced in U.S. from processing about 15.4 x 10^6 tons of bauxite in 1972, 94% of the alumina was utilized to make aluminium (Saxton and Kramer, 1975).

7.2 BAUXITE PROCESSING

Bauxite is composed mainly of metallic oxides with aluminium oxide comprising from 20% to 60% of the ore as mined. Approximately 87% of the bauxite ore is imported, mainly from Jamaica and Surinam. The many environmental problems associated with bauxite mining and shipping are caused by fugitive dust and water runoff. Bauxite ore may contain up to 30% moisture and should be dried at 110°C before shipping.

An overview of the Bauxite processing is shown in Figure 7.1.

The raw bauxite ore is benefacted by grinding to about 100 mesh, digested in caustic at elevated temperatures and pressures (145°C and 60 psig), and then filtered or thickened in the presence of flocculants. These operations yield a

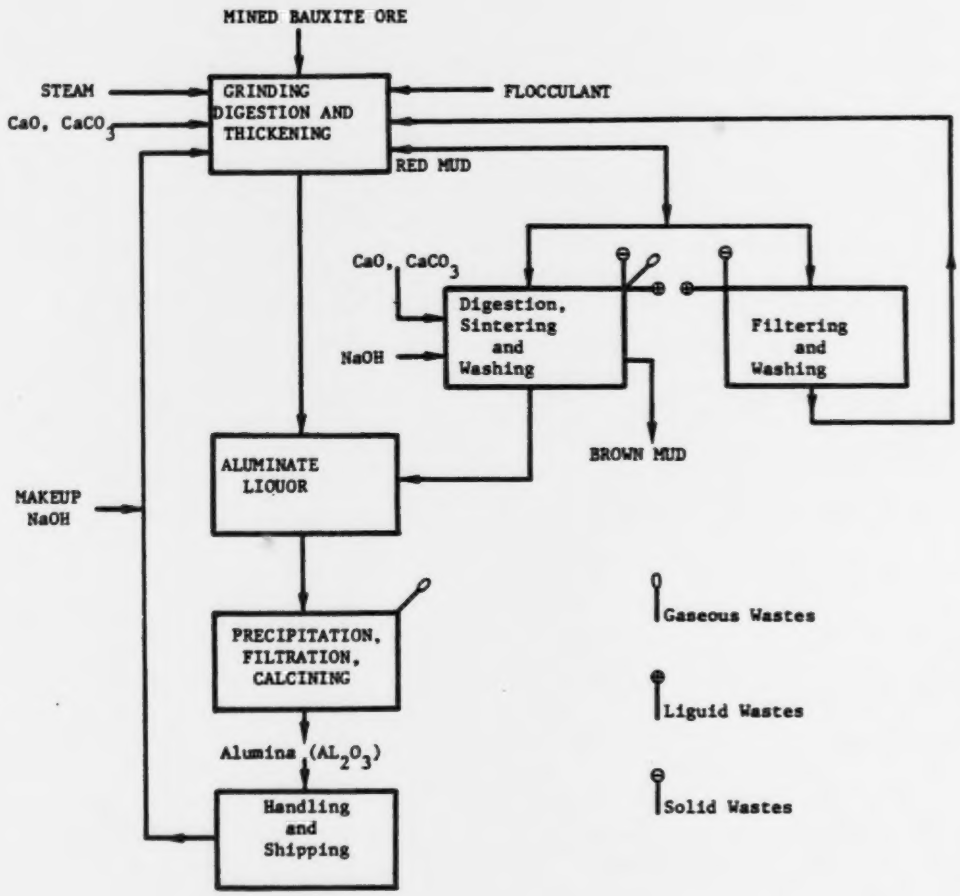
MINED BAUXITE ORE
STEAM
CaO, $CaCO_3$
GRINDING DIGESTION AND THICKENING
FLOCCULANT
RED MUD
CaO, $CaCO_3$
NaOH
Digestion, Sintering and Washing
Filtering and Washing
BROWN MUD
ALUMINATE LIQUOR
MAKEUP NaOH
PRECIPITATION, FILTRATION, CALCINING
Alumina (AL_2O_3)
Handling and Shipping
Gaseous Wastes
Liquid Wastes
Solid Wastes

Figure 7.1. Bauxite Processing

sodium aluminate liquor and a waste stream of "red mud" which contains the impurities found in the bauxite ore.

The aluminate liquor is diluted and cooled to hydrolyze the sodium aluminate, forming a precipitate of aluminium hydroxide which is filtered and calcined to alumina. The alumina is then shipped to aluminium smelting if so desired. Depending on the type of Bauxite processed, 1/3 to 2 kg of red mud is produced per each kilogram of alumina product. Table 7.1 gives the chemical analysis of red mud slurries from different bauxite ores (U.S. EPA, Oct. 1974). The pH of this slurry is approximately 12.5.

TABLE 7.1. CHEMICAL ANALYSIS OF RED MUDS

	Weight %		
Component	Arkansas	Surinam	Jamaica
Fe_2O_3	55-60	30-40	50.54
$A\ell_2O_3$	12-15	16-20	11-13
SiO_2	4- 5	11-14	2.5-6
TiO_2	4- 5	10-11	--
CaO	5-10	5- 6	6.5-8.5
Na_2O	2	6- 8	1.5-5.0

In the combination process, bauxite ores with high silica content, such as those from Arkansas, the red mud residue is treated to extract additional amounts of alumina and to recover sodium values. This additional extraction step is accomplished by mixing red mud with limestone and $(Na)_2CO_3$, and then sintering this mixture at 1100 to 1200°C. The important reactions are the conversion of silica to calcium silicate and residual alumina to sodium aluminate. The sintered products are leached to produce additional sodium aluminate solution, which is either filtered and added to the main stream for precipitation or is precipitated separately. By the addition of seed material and by careful control of composition and agitation, alumina trihydrate is precipitated in a controlled form.

The ideal solution to the red mud problem would be to develop a use for it. A possible application utilizes the high iron content of the red mud (Table 7.1). Fursman, et al. (1970) described a process based on sintering the red mud with carbon and limestone and melting the sinter in an electric ore furnace to produce a low priority iron which could be further processed into steel. This process was further developed (Guccione, 1971) but has not yet found commercial application. Other investigators have examined the applicability of red mud to manufacture portland cement, bricks, and road construction (Fursman, et al. 1970; Solyman and Briudoso, 1973).

There is a need to develop an economically viable leaching and extraction process for the recovery of mineral values from red mud wastes.

During the handling and shipping of alumina, dust is formed. The tendency of aluminas to form dust during handling depends on the degree of calcination and on the particle size distribution. The size distribution and adsorption capability of calcined alumina are important in the reduction and dry gas cleaning stages of aluminium manufacture, as will be discussed later.

With highly calcined, flowing aluminas, the formation of dust is prevented by the surface roughness, which increases as the α-alumina content rises. If fine grained hydroxide is calcined to a lower degree, it will start developing dust. The tendency of weakly calcined aluminas to cause dusting is counteracted by minimizing the amount of fines. This is normally done in the precipitation area of the Bayer process, where the particle size distribution of the hydroxide is controlled.

Decisive for the mechanical strength acquired by the individual hydroxide particles are (Schmidt, 1980):

- The basic principle applied for crystallization, i.e., nucleation, crystal growth, or agglomeration conditions
- Influence of liquor impurities such as $CaCo_3$ oxalates etc.
- The mechanical stresses to which the hydroxides are exposed during precipitation.

Schmidt, et al. (1980) reported that the gas/solid velocities and thermal stresses in the fluid bed calciner and in the rotary kiln have a strong influence on the particle size distribution of the calcined alumina.

Thus a detailed research program to improve the mechanical strength, adsorption capability and particle size distribution of calcined alumina by modifying the precipitation and calcining of alumina is suggested.

Studies conducted in the USSR and elsewhere indicate the possibility of using nitric acid stripping for the extraction of alumina from ores containing high amounts of silica. Sutyrin and Zverev (1976) reported that stripping at 160°C lowered acid usage and produced solutions less contaminated by iron. Acid stripping of domestic U.S. ores which contain high amounts of silica should be optimized by proper control of the stripping temperature.

The enrichment of high silica bauxite ores using heterotrophic bacteria is reported by Andreev, et al. (1976). It was possible to produce a concentrate with 48.4% $A\ell_2O_3$ content at a recovery of 74%. Thus, additional research is needed to develop acid stripping and bacterial enrichment of domestic bauxite ores.

7.3 PRIMARY ALUMINIUM SMELTING

The large scale, economic production of primary aluminium became possible when, in 1886, C.M. Hall and P. Heroult independently developed the electrolytic process which has remained essentially unchanged, except for improvements in equipment design and operating practices, it is used in all the commercial processes in U.S. producing primary aluminium. There are 31 aluminium reduction plants in the U.S. with a total annual capacity of about 4.5×10^6 tons. The energy consumed annually at full production is estimated to be in the range of 80 to 100 billion K.W.H.

The basic process for reducing alumina to aluminium is shown schematically in Figure 7.2.

The raw materials used in the aluminium production include alumina, cryolite (a double flouride of Na and $A\ell$), pitch, petroleum coke, and aluminium flouride. For every kg of aluminium produced, about 2 kg alumina, 0.25 kg pitch, 0.05 kg cryolite, 0.5 kg petroleum coke, 0.04 kg aluminium flouride, 0.6 kg baked carbon and 22 K.W.H. of electrical energy are needed.

The heart of the aluminium plant is the electrolytic cell, which consists of a steel container lined with refractory brick with an inner lining of carbon. The cells are arranged in rows, in an operating unit (potline) as many as 100 to 250 cells are electrically connected in series. The electrical supply is direct current and is on the order of several hundred volts and 60,000 - 100,000 amperes. The carbon lining at the bottom of the cell acts as a cathode when covered with molten aluminium. The anode of the cell is baked carbon. The electrolite consists of a mixture of

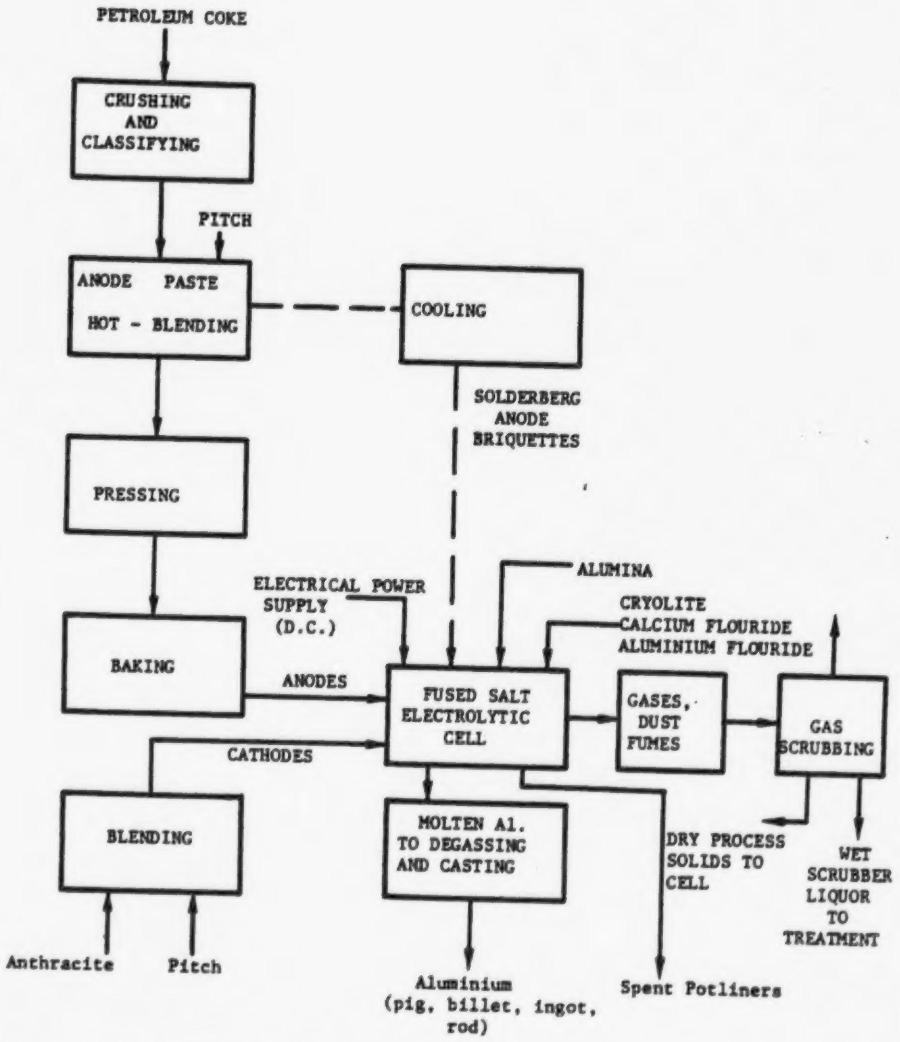
PETROLEUM COKE
CRUSHING AND CLASSIFYING
PITCH
ANODE PASTE HOT - BLENDING
COOLING
SOLDERBERG ANODE BRIQUETTES
PRESSING
ELECTRICAL POWER SUPPLY (D.C.)
ALUMINA
CRYOLITE
CALCIUM FLOURIDE
ALUMINIUM FLOURIDE
BAKING
ANODES
FUSED SALT ELECTROLYTIC CELL
GASES, DUST FUMES
GAS SCRUBBING
CATHODES
BLENDING
MOLTEN Al. TO DEGASSING AND CASTING
DRY PROCESS SOLIDS TO CELL
WET SCRUBBER LIQUOR TO TREATMENT
Anthracite
Pitch
Aluminium (pig, billet, ingot, rod)
Spent Potliners

Figure 7.2. Primary Aluminium Production.

cryolite (80-85% by wt.), calcium flouride (5-7%), and alumina (2-8%). Alumina is added to the bath intermittently to maintain the concentration of dissolved alumina within the desired range. The fused salt bath is usually at a temperature of 900°C.

The reaction in the aluminium reduction cell is not completely understood (Kirk-Othmer, 1963). Apparently aluminium is reduced from the trivalent state assuming ionization in the molten salt, to the liquid metal state at the cathode. Oxygen, assumed present in the bath in the divalent state appears at the carbon anode and immediately reacts with the anode and forms a mixture of CO_2 (≈75%) and CO (≈25%).

Thus, the operation of the electrolytic aluminium reduction cell results in the continuous consumption of alumina and the carbon anode, and the evolution of gaseous reaction products. The aluminium is withdrawn intermittently from the bottom of the molten bath and is collected in ladles and cast into ingots.

The various anode making operations are conducted in the anode paste plant. The anode paste consists mainly of high grade coke (petroleum and pitch coke) and pitch, with a maximum of 0.7% ash, 0.7% sulfur, 8% volatiles, 0.5% alkali and 2% moisture. The two types of pitch handling systems are, solid pitch handling and liquid pitch handling (using organic liquids as a heat transfer medium). Dust and toxic emissions are the main pollutants from these systems.

The two different anode systems used differ in the replacement of the anode.

1. Prebaked system - the anode is replaced intermittently,
2. Solderberg system - the anode is replaced continuously by the anode paste descending from the anode shell suspended above the electrolytic cell.

The carbon cathode has an average life of between 2-3 years. The spent cathode lining is removed by drilling and/or soaking in water. About 1200 m^3 of shell waste is generated each year in the U.S.

The major pollutants generated during the smelting of alumina include particulate emissions, inorganic flourides, oxides of sulfur, H_2S, carbon disulfide, carbonyl sulphide, CO and CO_2, and spent carbon cathode.

Emissions from the horizontal-stud Solderberg cell and vertical-stud Solderberg cell (Kotari, et al. 1974) are shown in Table 7.2.

TABLE 7.2 EMISSIONS FROM SOLDERBERG CELL

Cell Type	Emissions	lb. per ton of Aluminium
Vertical-stud Solderberg	Particulates	98.4
	Gaseous Flourides (HF)	26.6
	Particulate Flouride	15.6
Horizontal-stud Solderberg	Particulates	78.4
	Gaseous Flourides(HF)	30.4
	Particulate Flouride	10.6

The particulates contain $A\ell_2O_3$, Na_2CO_3 and carbon dust. Approximately 60% of the particulates are less than 5 μm in size. Increasing the mechanical strength of $A\ell_2O_3$ by modifying precipitation and calcination operations (as discussed earlier in this section) may lead to a reduction of particulate $A\ell_2O_3$ emissions.

The emissions of both particulate and flourine compounds from the bath increase with increasing temperature, decreasing alumina content, and decreasing bath ratio of $NaF/A\ell F_3$ (Kotari, et al. 1974). The hydrogen flouride emissions are generated primarily as a result of moisture treating with $A\ell F_3$ containing materials. The HF emissions increase directly with the water (Bell and Dawson, 1971). The sources of moisture are from the atmosphere, the moisture content of $A\ell_2O_3$.

The flouride particulates range in size from about 0.05 - 0.75 μm with the majority of the particles smaller than 0.25 μm (McCabe, 1975). The flourine content of the total gases, withdrawn from the pots or pot rooms may vary from 2 to 40 mg/ft^3, or between 18.97 - 25.63 kg/ton of the raw material (Kotari, et al. 1974). Cooling the process by 5^oC will reduce flourine consumption by 0.2 kg/ton of raw material (Kotari, et al. 1974). An optimization of the operative temperature of the electrolytic cell is needed to minimize the generation of hydrogen flouride. Fifteen percent of the flouride present in the emissions from prebaked pots occurs as HF, while 90% of the flouride in Solderberg pot emissions occurs as HF (Less and Waddington, 1971).

found that the maximum adsorption capacity determined in the laboratory is roughly twice that determined under production conditions. Research efforts are needed to explain this discrepancy between laboratory and production tests and thereby improve the adsorption of HF on $A\ell_2O_3$ in industrial pollution control devices. Any increase in the surface area of $A\ell_2O_3$ per unit weight would increase its HF adsorption capacity.

Sulfur oxides in the fumes from electrolytic cells are generally removed by wet scrubbing (in lime scrubbers) and/or by dry scrubbing (by adsorption on $A\ell_2O_3$). It is reported (U.S. EPA, Dec. 1973) that a venturi type lime scrubbing system at the Mitsui Aluminium Company, Ltd. has operated at SO_2 removal efficiencies of 86%-93% for more than a year. It may be necessary to improve on the venturi contacting device to improve SO_2 removal efficiencies or to use additional dry scrubbing units to further remove SO_2.

The low equilibrium value of SO_2 adsorption on smelter grade $A\ell_2O_3$ is a limiting factor in the removal of SO_2 from cell gases in a dry scrubber. It was shown by Lamb (1979) that the presence of adsorbed flouride from cell gas would reduce equilibrium adsorption of SO_2 even further. This effect will be most important with vertical stud Solderberg cells where HF loading and concentration is higher than the horizontal stud Solderberg or prebaked electrolytic cells. It is necessary to understand the interaction of SO_2 and HF on $A\ell_2O_3$ to develop dry scrubber systems to remove SO_2.

Henry (1963) reported on experimental work which established correlations between three cell operating parameters and effluent production. The results of these experiments are summarized in Table 7.3.

TABLE 7.3. EFFECT OF CELL OPERATING PARAMETERS AS FLOURIDE EFFLUENT

Range of Variables			Effect on Flouride Effluent
Cryolite Bath Ratio ($NaF/A\ell F_3$)	Alumina Content	Temp. °C	
1.44 to 1.54	4%	975°C	31% decrease
1.50	3% to 5%	975°C	20% decrease
1.50	4%	982°C	24% decrease

It was thus shown that by increasing the bath ratio ($NaF/A\ell F_3$), the alumina content of the bath, and decreasing the cell temperature, a decrease was seen in the flouride content of the cell effluent. Research efforts should be directed to modify these cell operational variables in order to minimize flouride production.

There has been several research efforts directed at the reduction of fume treatment by adsorbing HF on alumina. Investigations carried under production conditions (Colpitts, 1972; Chavinean and Muhlrad, 1973; Cochran, 1974) show that the efficiency of the adsorption process falls off once a certain quantity of gaseous flourine has been adsorbed, and that this quantity is directly proportional to the specific surface area of $A\ell_2O_3$. In a recent study, Baverez and DeMarco (1980) showed that HF is adsorbed on $A\ell_2O_3$ as two bimolecular layers. They

The possibility of the use of chemical additives to remove sulfur in the coal as slag is another research area that is being investigated by Alcoa (West, 1980) under a contract with the DOE. Alkali additives and K_2CO_3 are known to achieve high efficiencies in removing SO_2.

Tschopp, Franke and Bernhauser (1979) report that additions of Lithium reduced the operating temperature of the electrolytic cell by 14°C and reduced flourine evolution by 25%, based on their studies at a Swiss aluminium plant at Essen.

The used cell linings consist largely of carbon (the cathode), but also contain cryolite, aluminium carbide, and aluminium nitride. NaOH and sodium cyanide also appear in waters resulting from leaching of cell linings. The carbides react with water vapor in the air to produce methane (CH_4), hydrogen, C_2H_2 and other hydrocarbons. The nitride yields ammonia. This cathode material, in the past, has been dumped or used as landfill. However, environmental concerns now consider the flouride content to pose a possible pollution hazard. Over 30% of the flouride in scrapped cell linings is water soluble. Lu and Shelley (1970) describe eleven treatment methods to treat cell linings. They concluded that apart from the two methods, sodium hydroxide leaching and steam hydrolysis, already in commercial use, the most promising approach seems to be the use of hot water hydrolysis and recycle of treated cathode material. However, it is unlikely that all the cathode carbon can be recycled, the problem of flourides and cyanides in unused cathode still remains. It is necessary to develop leaching methods to remove flourides and cyanides to facilitate disposal of cathode linings.

Table 7.4 gives the major pollution problems associated with the Primary Aluminium Industry.

7.4 RECOMMENDED RESEARCH STUDIES FOR POLLUTION CONTROL IN THE PRIMARY ALUMINIUM INDUSTRY

After evaluating the available literature, the following areas are recommended for further research by the study:

- Leaching and extraction of red mud to recover mineral values.
- Improving the mechanical strength, adsorption capacity and particle size distribution of calcined alumina by optimizing precipitation and calcination of alumina.
- Optimizing the temperature for and stripping of high silica U.S. Bauxite ores.
- Enrichment of high silica U.S. Bauxite using bacterial action.
- Improving calcination of $A\ell_2O_3$ to reduce its moisture content thereby reducing formation of HF from electrolytic cells.
- Optimization of the cryolite bath ($NaF/A\ell F_3$) ratio, alumina content and temperature of cell to reduce flouride emissions.
- Increasing the adsorption capacity of $A\ell_2O_3$ to

Table 7-4. Suggested Process Modifications for Pollution Control in the Primary Aluminium Industry.

Process	Pollutants	Source in Process	Nature of Pollutants	Suggested Process Modifications
Bauxite Processing	Red Mud	Ore Digestion	Fe_2O_3, Al_2O_3, - etc. oxides	Recovery of mineral values, Developing alternative Uses for red mud.
Handling and Shipping	Alumina	-----------	Particulates	Optimizing precipitation and calcination to improve mechanical strength and particle size distribution of alumina.
Primary Aluminium Smelting	Alumina	Electrolytic Cell	Particulates	Optimizing precipitation and calcination to improve mechanical strength and particle size distribution of alumina.
Primary Aluminium Smelting	Flourides	Electrolytic Cell	HF	Improving calcination of Al_2O_3 to decrease moisture content; optimizing cryolite bath ratio, alumina content and temperature of cell; use of lithium as additive; and, increasing adsorption capacity of Al_2O_3.

Table 7-4. Suggested Process Modification for Pollution Control in the Primary Aluminium Industry. (Cont'd)

Process	Pollutants	Source in Process	Nature of Pollutants	Suggested Process Modificiations
Primary Aluminium Smelting	SO_x	Electrolytic Cell	-----------	Improving adsorption of SO_x on $A\ell_2O_3$ in the presence HF; Use of additives to remove sulfur in coal as slag.
Primary Aluminium Smelting	Spent Cathode Linings	Electrolytic Cell	Carbon, cryolite, aluminium carbide aluminium nitride, cyanides and flourides	Leaching to remove cyanides and flourides; and hot-water/steam hydrolysis and sodium hydroxide leaching to recycle spent cathode.

remove HF in the fumes from electrolysis.

- Understanding the interaction of HF and SO_x on Al_2O_3 to improve dry scrubbing of SO_x gases from the electrolytic cell.
- The effect of various additives in removing sulfur in coal as slag.
- Effect of adding Lithium on cell operating temperature and HF emissions.
- Leaching of cathode linings to remove flourides and cyanides.

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CHAPTER 8

PHOSPHATE FERTILIZER INDUSTRY

8.1 INTRODUCTION

Fertilizers in general can be categorized by their composition of plant nutrients. The fertilizers differ in their composition of plant nutrients of nitrogen, phosphorous, and potassium. Normal superphosphate contains only one nutrient, phosphorous. Ammonium phosphate contains phosphorous and nitrogen. Generally, the solid and liquid mix fertilizers contain all three nutrients in varying amounts.

Over 44 million metric tons of phosphate rock were mined in the United States during 1975. Approximately 22.75 million metric tons were consumed by the fertilizer industry during the same period (Nyers, et al. 1979).

The phosphate based fertilizers are produced by conversion of unsoluble phosphate ore into the soluble form necessary for plant consumption. The phosphoric acid, backbone of phosphate fertilizer, is formed by mixing phosphate rock with sulfuric acid.

This chapter concentrates on the production of phosphoric acid, normal superphosphate, and ammonium phosphate. The preparation of phosphate rock is not discussed in this chapter.

8.2 WET PROCESS PHOSPHORIC ACID PRODUCTION

Most of the phosphoric acid in the fertilizer industry is prepared by the wet process. In this process phosphate rock reacts with sulfuric acid to form phosphoric acid and gypsum. The overall chemistry of this reaction is shown in equation 8.1 (Corbridge, 1978):

$$\begin{array}{l} \underset{\text{(Flourapatite)}}{Ca_{10}(PO_4)_6F_2} + 10\ H_2SO_4 + 20H_2 \rightleftarrows \\ \qquad \underset{\text{(gypsum)}}{6H_3PO_4} + 2HF + 10CaSO_4 + 2H_2 \end{array} \qquad (8.1)$$

Phosphoric acid is the most important intermediate in the production of phosphate fertilizer. In addition to its use in the production of ammonium phosphates and concentrated superphosphate, it is an intermediate for mixed fertilizer, both liquid and solid (Nyers, et al. 2979).

A simplified flow diagram of the wet process for phosphoric acid production is given in Figure 8.1. The process consists of three steps: (1) reaction of phosphate rock, (2) separation of acid from the sulfate, and (3) concentration of the acid. Important variables for a successful operation are type of phosphate rock used, the temperature of the reaction, and the slurry density controlled by recycling weak acid to the digester step.

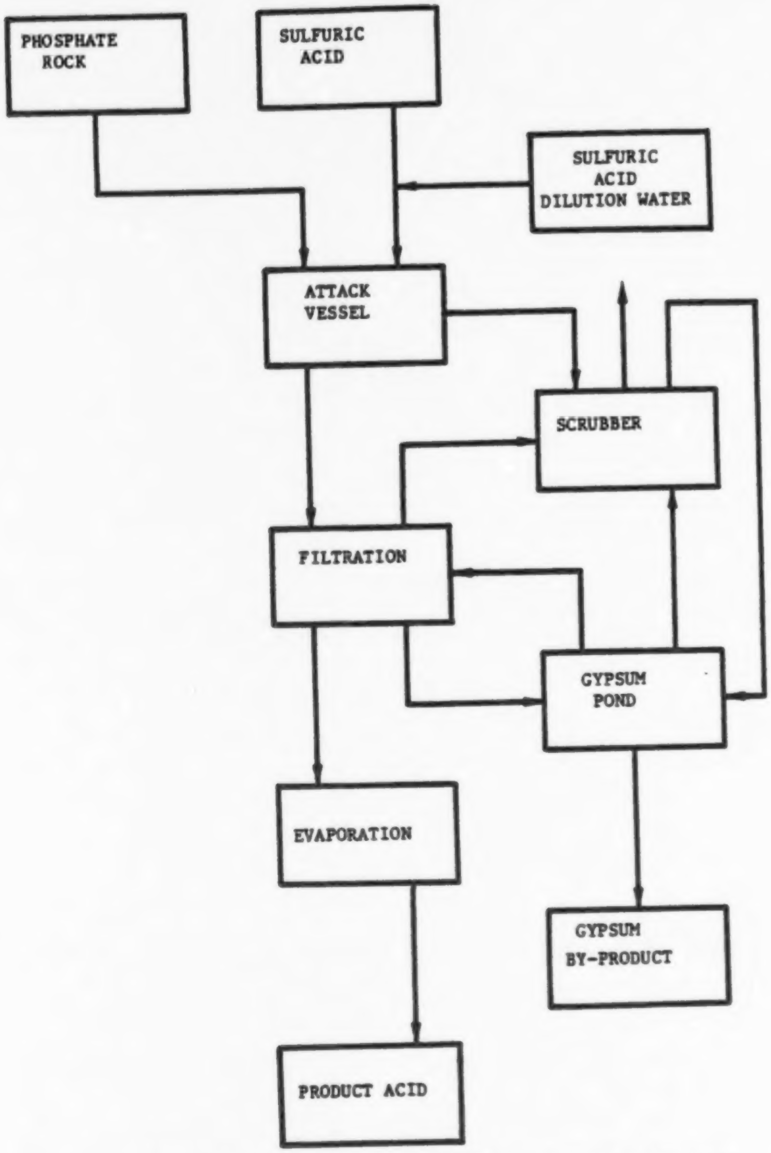
PHOSPHATE ROCK
SULFURIC ACID
SULFURIC ACID DILUTION WATER
ATTACK VESSEL
SCRUBBER
FILTRATION
GYPSUM POND
EVAPORATION
GYPSUM BY-PRODUCT
PRODUCT ACID

Figure 8.1. Wet Process Phoric Acid Production Process (Nyers, *et al.* 1979).

→ phosphoric

Most wet process plants employ the crystalization of calcium sulfate in the dehydrated state as opposed to hemi-hydrate or anhydrate. This is due to the fact that the dehydrate process does not impose as many operating problems as the hemi-hydrate or anhydrate process. Acid produced by the dehydrate process contains about 13% Phosphorus (P) (30% P_2O_5) and is generally concentrated to 17 to 24% P (40 to 54% P_2O_5) before use. The concentration of phosphoric acid is facilitated by continuous heated vacuum evaporators (Olson, et al. 1971).

There is a substantial amount of pollutants evolved by the wet process. A large portion of reactants become by-products contributing to the pollution. The main by-product of the dehydrate process is the impure gypsum of little practical use. Phosphate rock is composed of 2/3 gypsum, thus making the disposal of the by-products a formidable problem. The other by-product is flouride, which evolves during digestion of phosphate rock and can be recovered with water by a relatively simple scrubbing procedure.

The evolution of gaseous flouride is caused by any flouride containing liquid due to the vapor pressure of flouride. The emission rate varies with temperature, concentration, absolute pressure, and exposed area of the liquid surface on the digester. Gaseous flouride emissions contain silicon tetraflouride, which is formed by the reaction of hydrogen flouride in the reactor. Tetraflouride formation is favored at temperatures below 100°C (Nyers, et al. 1979).

Poorly controlled wet process phosphoric acid (WPPA) plants may have emissions as high as .07 pound of flouride/ton of P_2O_5 fuel. On the other hand, well controlled plants using packed scrubbers or other equally effective control devices can achieve flouride emissions below .02 pound/ton of P_2O_5 input (U.S. EPA, Oct. 1974). The data indicates that the emission factors for plants that use flouride recovery is not significantly different from those plants that employ the recovery. The recovery refers to flourine recovered as fluosilicic acid, flourides, flousilicates, or other by-products (Nyers, et al. 1979).

The final flourine emission is strongly dependent on the type of scrubber used, scrubber operation, and use of fresh water tail gas scrubbers. Plants that use flourine recovery may dispose less volatile flourine to their pond system, thus having fewer emissions from the ponds.

The most important emission source in the typical WPPA process is the ventilating air from the digester. The digester vent gases contain water vapor, particulate dust, and SiF_4. The removal of flourine can be accomplished by the wet process or adsorption (solid reagent or adsorption system) of the ventilating air. The wet process has been used exclusively, however, the advantages and capabilities of the adsorption process should be studied (U.S. EPA, March 1973).

The design of the scrubbing equipment is limited by the chemistry of the reactions between the gypsum pond water and the flourine containing gases discharged from the WPPA plant reactor. The following reactions occur in the reactor:

$$CaF_2 + H_2SO_4 \rightleftarrows CaSO_4 + 2HF \tag{8.2}$$

or

$$2HF + SiF_4 \rightleftarrows H_2SiF_6 \tag{8.3}$$

Furthermore, hydrolysis of SiF_4 can occur at high concentrations (i.e. higher than equilibrium concentration) as follows:

$$3SiF_4 + 4H_2O \rightleftarrows Si\,(OH)_4 + 2H_2{+}SiF_6 \tag{8.4}$$

As a result of this reaction, a gelatinous deposit of polymeric silica is formed, which tends to plug the scrubber packings (U.S. EPA, March 1973).

The three most effective scrubbing techniques for removal of flourine are: (1) counter-current, (2) co-current and, (3) cross-flow scrubbing. Counter-current scrubbers have the highest potential removal efficiency since it contacts the gas leaving the scrubber with incoming clean liquor. However, co-current scrubbing is less prone to plugging and requires a lower gas pressure drop to operate. The crossflow scrubber is a compromise between the counter and co-current scrubbers, it employs the efficiency of the former with the mechanical advantages of the latter. The cross-flow scrubber has been used in combination with spray towers, venturi, or wet cyclones in phosphoric acid plants (U.S. EPA, March 1973).

The efficiency of the scrubber is dependent on the temperature and composition of the scrubber medium. The gypsum pond water used in the scrubber contains 3000 ppm to 10,000 ppm of flourine (Nyers, _et al_. 1979). Efficient removal of flourine from the gas stream is reduced, due to the high partial pressure of hydrogen flouride in the pond water. The mass transfer rate also decreases as temperature increases, thus, fresh water should be used as the scrubbing medium in the last stage of scrubbing.

Oxides of sulfur are also emitted in the WPPA process. Their production ranges from 0.0077 to 0.058g/kg P_2O_5. However, the origin of SO_x formation is not clear in the WPPA process (Nyers, _et al_. 1979). The cause of its emission must first be determined before any measure regarding its reduction within the process is taken.

8.3 RECOMMENDED AREAS FOR POLLUTION CONTROL RESEARCH: WET PROCESS PHOSPHORIC ACID PRODUCTION

After evaluating the available literature, the following areas are recommended for further research by the study:

- Studies on purification of phosphate feed to reactor to reduce impurities which cause by-product formation.
- Comparative studies on adsorption and absorption of flourine to determine the most efficient technique to alleviate flourine emission.
- Research on the design and operating parameters of the scrubber to reduce plugging and increase the rate of flourine transfer from the vent gases to scrubbing medium.

8.4 NORMAL SUPERPHOSPHATE PRODUCTION

Normal superphosphate (NS) is produced by the reaction of phosphate rock with sulfuric acid. The phosphate rock and H_2SO_4 are mixed in a cone mixer (reactor vessel), the acidulate is then transfered to an enclosed area (den) to solidify. The solidified product is then stored for curing. The schematic diagram of this process is shown in Figure 8.2.

The NS production can be accomplished by both continuous and batch processes. For the batch process, a pan mixer (instead of cone mixer for the continuous process is used. However, both processes convert fluorapatite in the rock to soluble monocalcium phosphate. The major reaction in this process is:

$$[Ca_3(PO_4)_2]_3 + CaF_2 + 7H_2SO_4 + 3H_2O \rightleftarrows 3[CaH_4(PO_4)_2 H_2O] + 7CaSO_4 + 2HF \qquad (8.5)$$

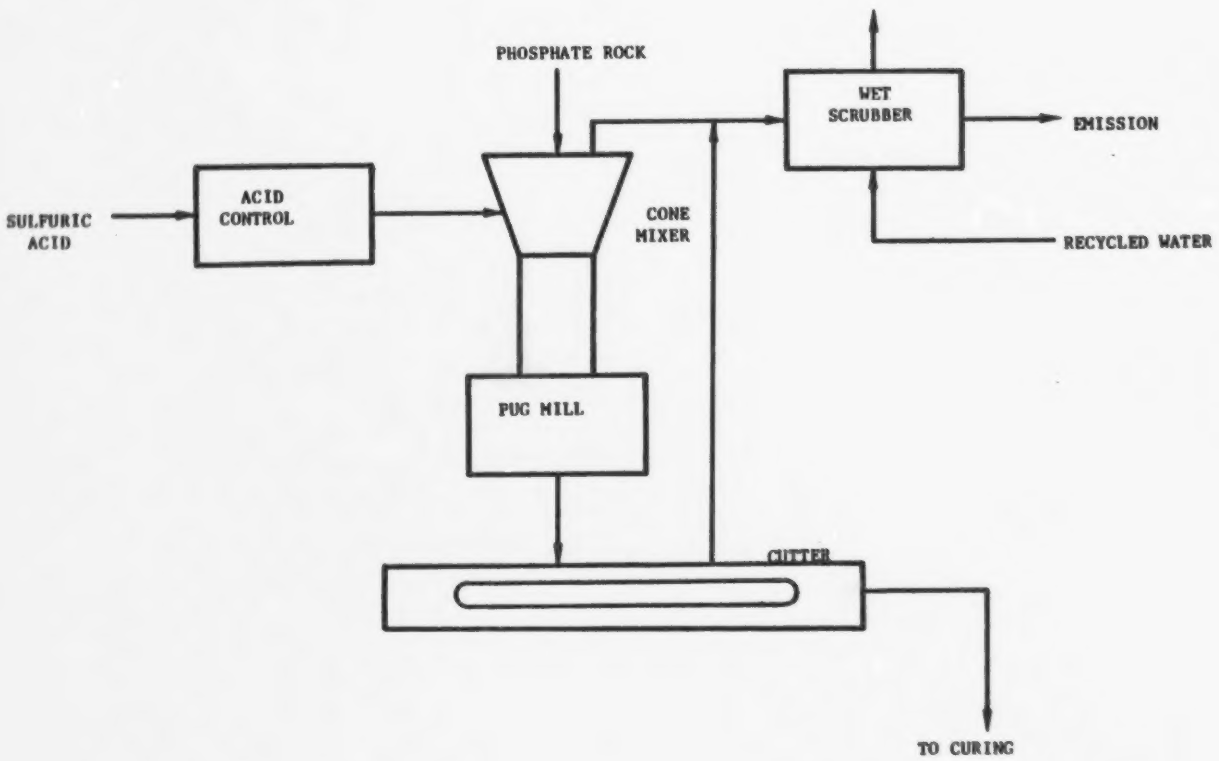
PHOSPHATE ROCK
SULFURIC ACID
ACID CONTROL
CONE MIXER
WET SCRUBBER
EMISSION
RECYCLED WATER
PUG MILL
CUTTER
TO CURING

Figure 8.2. Flow Chart of Normal Superphosphate Production Process (Nyers, et al. 1979).

The source of pollution emissions for a NS plant are the mixers, den, and curing building. Between 1.5 kg and 9.0 kg of flourides/metric ton of NS are released during production and the curing process (Nyers, et al. 1979). The flouride emissions occur in form of flouride vapor evolving as hydrogen flouride and silicon tetraflouride. The flouride emissions range from 0.07 g F/kg P_2O_5 to 0.45 g F/kg P_2O_5. Individual emission rates from each unit is hard to find since all gases are vented to the same stack.

As previously discussed, the scrubbing is inhibited by the formation of a gelatinous mass, generated by the reaction of tetraflouride and water. Thus, the use of conventional scrubbing, for pollution abatement, is greatly influenced by this reaction. The effectiveness of the flouride reduction by a scrubber is determined by inlet flourine concentration, outlet saturation temperature, composition and temperature of the scrubbing liquid, scrubber type and transfer units, and effectiveness of entrainment separation (Heller, et al. 1968).

The best strategy for pollution control is to use a crossflow scrubber. Furthermore, flourine removal is enhanced by use of fresh water in the last stage and increasing the number of stages in the scrubber (Nyers, et al. 1979).

8.5 RECOMMENDED AREAS FOR POLLUTION CONTROL RESEARCH: NORMAL SUPERPHOSPHATE PRODUCTION

After evaluating the available literature, the following areas are recommended for further research by the study:

- Studies on the scrubber design and optimal operating parameters to reduce flourine emissions.

8.6 AMMONIUM PHOSPHATE PRODUCTION

The production of ammonium phosphate (AP), mostly diammonium phosphate (DAP), has increased rapidly in the past 3 decades. The total of ammonium phosphate produced in the U.S. reached nearly 3.7 million tons P_2O_5, which is 63.4% of all phosphate fertilizers produced in the U.S. (Kirk-Othmer, 1980). Approximately 99% of AP are used as fertilizer (Nyers, et al. 1979).

The discussion to follow includes the granulation of phosphoric acid with anhydrous ammoniation-granulation to produce granular fertilizer. Ammonium phosphate is produced by the reaction of phosphoric acid with anhydrous ammonia. In 1975, 84% of AP produced in the U.S. was of DAP grade (i.e. percentage of available N-K-P is 16-0-48 (Nyers, et al. 1979).

Ammonium phosphate $[(NH_4)_2HPO_4]$ is produced by the reaction of 1 mole of phosphoric acid with 2 moles of ammonia forming a product with 21.1% nitrogen and 54% available phosphorous. Monoammonium phosphate (MAP) can also react with ammonia to yield DAP. The DAP production can be performed in either a pugmill or rotary drum ammoniator. Approximately 95% of ammoniation granulation plants in the U.S. use rotary drum-mixer developed by TVA (Rawlings and Reznik, 1976).

The pollution sources arise from four operations in the ammonium production process: (1) reactor, (2) ammoniator, (3) dryer, and (4) cooling. Typical emissions include, ammonia, flouride, particulates, and negligible amount of combustion gases. The following discussion is for the TVA process depicted in Figure 8.3.

The reactor or preneutralizer is a vessel into which 70% of ammonia and all of the phosphoric acid is introduced. The reactor operates at atmospheric pressure and 100-120°C. The $NH_3:H_3PO_4$ ratio is maintained at 1.3:1 to 1.5:1 for maximum solibility of MAP, which is the main product of the reactor (Nyers, et al. 1979).

The emissions from the reactor contain ammonia and flourides in form of gaseous emissions. The emissions are caused by volatilization due to incomplete chemical reactions and excess free ammonia. Collective emissions for reactor and ammoniator-granulator are as follows:

Flourides (as F)	0.023g/kg P_2O_5
Particulate	0.076g/kg P_2O_5

Ammonia emission data is available for the AP production as a whole (Nyers, et al. 1979).

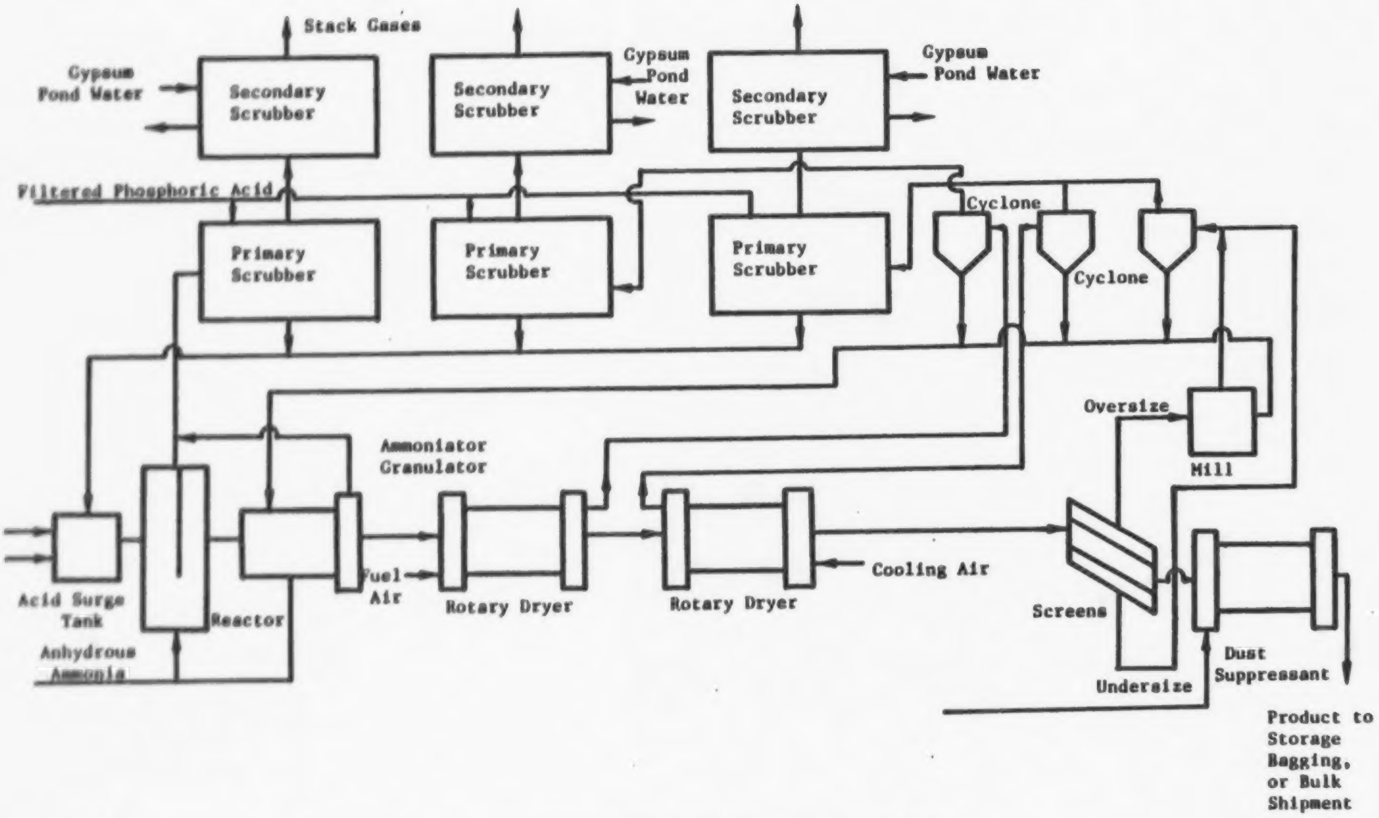
Stack Gases
Gypsum Pond Water
Secondary Scrubber
Secondary Scrubber
Gypsum Pond Water
Secondary Scrubber
Gypsum Pond Water
Filtered Phosphoric Acid
Primary Scrubber
Primary Scrubber
Primary Scrubber
Cyclone
Cyclone
Oversize
Mill
Ammoniator Granulator
Acid Surge Tank
Reactor
Anhydrous Ammonia
Fuel
Air
Rotary Dryer
Rotary Dryer
Cooling Air
Screens
Undersize
Dust Suppressant
Product to Storage Bagging, or Bulk Shipment

Figure 8.3. Flow Diagram for TVA Ammonium Phosphate Process. (Myers, et al. 1979).

The reactor emissions can be controlled with a more efficient design of the reactor. In theory, the reactor can be designed without any ventilation, but in practice they are operated at a 57 - 76 cfm ventilation rate (U.S. EPA, March 1973).

The reactor design can be modified to reduce the ventilation rate and thus the atmospheric emissions. Furthermore, the excess ammonia should be avoided in the reactor vessel. The rate of reaction should be increased catalytically by changing the process conditions, and/or the residence time should be increased in order to achieve complete reaction.

The granulation by agglomeration and by coating particles with slurry from the reactor takes place in the rotating drum. Ammonia is supplied by a sparging action underneath the bed to bring the $NH_3:H_3PO_4$ ratio to 1.8:1.0 to 2.0:2.0 (U.S. EPA, March 1973). The granulation can, theoretically, be performed with no ventilation. The ventilation is mainly a function of design of the granulator, thus design considerations play an important role in the final emissions of ammonia.

The emission from the reactor and granulator are scrubbed for pollution reductions. Anyone of the various scrubbing techniques can be applied to these off gases. However, packed scrubbers should be avoided due to the formation of gelatinous silicon or DAP, which tend to plug the scrubber. The best scrubbing technique for primary scrubbing is a venturi cyclone scrubber which has good capabilities for absorption of ammonia and particulate matter.

Moist granules of DAP are dried to 2% moisture in a counter-current gas or oil fired dryer unit. The controlled emissions from the dryer and cooler are 0.015g/kg P_2O_5 flouride and 0.75g/kg P_2O_5 particulate emissions (Nyers, _et al_. 1979).

The flouride emissions are due to the dissociation of the fertilizer product and particulate emissions are caused by entrainment of DAP and MAP dusts in the ventilation air streams. The particulate emissions may contain both ammonium flouride and ammonium phosilicates (U.S. EPA, March 1973). Typically, the primary scrubbers are designed to capture the particulates. Thus the design of the primary scrubbers must account for the particulate as well as removal of off gases from the ventilation streams. Furthermore, the scrubbing medium, in the primary scrubber, should be acidic enough to absorb the ammonium discharge. For this prupose 30% phosphoric acid solution is used for the primary scrubbing medium to recover ammonia (U.S. EPA, March 1973).

Whenever the use of only one scrubber is not sufficient to remove particulates and gases, combination of scrubbers must be considered.

Table 8.1 contains the summary of pollution problems associated with the phosphate rock industry and the suggested

Table 8-1. Pollutants and Suggested Strategy for Selected Phosphate Rock Fertilizer

Industry	Process	Pollutants	Sources in Process	Nature of Pollutants	Pollutant Control Strategy
Wet process phosphoric acid	Phosphate Rock Processing	Flourides Particulates, SO_x, & Gypsum.	Reactor vessel, filteration, vaporation, & gypsum pond	Inorganic gases, and solids	Crossflow scrubbing with fresh water in the last stage, and/or use combination of scrubbers.
Normal Super-Phosphate Production	Phosphate Rock Processing	Flourides, Particulates	Mixers, den, and curing.	Inorganic gases, and solids	Scrubbing the offgases, cross flow scrubbing, and/or use combination scrubbing
Ammonium Phosphate Production	Diammonium Phosphate Production	Ammonia, Flourides, and Particulates	Reactor, ammoniator, dryer, and cooler.	Inorganic gases, and solids	Use combination primary and secondary scrubbing improve the design on the reactor and ammoniator to reduce ventilation rate.

strategy.

8.7 RECOMMENDED AREAS FOR POLLUTION CONTROL RESEARCH: AMMONIUM PHOSPHATE PRODUCTION

After evaluating the available literature, the following areas are recommended for further research by the study:

- Research on kinetics of reaction of ammonia with phosphoric acid to enhance this reaction, either catalytically or by increasing the residence time in the reactor vessel, which would reduce the emission.
- Studies on design of the reactor vessel and granulators to minimize the ventilation rate which would lead to smaller volumes of gaseous emission.
- Research on the design and selection of optimal operating parameters for the scrubbing unit to reduce the ammonia, flouride, and particulate emissions.

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CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 INTRODUCTION

Based on the preparation of the reports submitted for the eight industries, it is concluded that research programs in the following areas should yield results encompassed in the objectives of this program.

9.2 SOLVENT EXTRACTION

Modification of solvent extractor design and operation would minimize metal ions or non phenolic organics in process streams leaving extractor batteries in hydrometallurgical and coal liquefaction processes respectively. Studies could include modelling of selective ion extraction in multiple metal systems, characterization of liquid dispersion properties such as surface area and droplet mixing as a function of power consumption, extraction kinetics, and separation of liquid-liquid dispersions.

9.3 CATALYST DEACTIVATION

Modification of catalyst reactor bed operation and studies on catalyst deactivation will increase catalyst life and reduce the volume of spent catalyst from coal gasification operations. Studies could include modelling catalyst deactivation phenomena as affected by temperature, pressure, feed gas composition, catalyst structure, and catalyst type. Optimal reactor operation studies for sulfur guard catalysts (ZnO), shift catalysts (cobalt-molybdate), and methanation catalysts (nickel) can be conducted.

9.4 LEACHING PROCESSES

Modification and improvement of leaching processes for sulfide or oxide ores will reduce ground water contamination and dissolved metal salts in process streams in hydrometallurgical processes. These results also apply to recovery of metals from particulates (smelting dust), coal liquefaction ash, spent catalysts in coal gasification, and coal liquefaction residues. Studies could include vat leaching using ammonial or in organic acid solutions. Characterization of kinetics of leaching as affected by particle size, temperature, concentrations and particle structure can be explored. Minimum power requirements to suspend particles and maximize particle-liquid mass transfer can be studied.

9.5 GAS ABSORPTION

Modification and improvement of gas absorption processes such as the Stretford absorption process will reduce emissions of H_2, HCN, and CO_2 in tail gases from coal liquefaction processes and H_2S and SO_2 for smelter off gas recovery operations. Studies could include gas-liquid mass transfer and gas-liquid reactions in absorption liquids (sodium metavanadate, sodium carbonate, sodium bicarbonate, and ADA) as affected by temperature, pressure, and gas-liquid contacting.

9.6 GAS-LIQUID-SOLID REACTIONS

Modification and improvement of reactors for contacting and reacting gas-liquid-solid dispersions would minimize particulate emissions in coal liquefaction reactions as well as vat leaching processes. Studies could include coal dissolution rates, gas dispersion, particulate agglomeration, dissolved gas-particle reactions, and determination of the rate limiting steps as affected by mechanical agitation, temperature, pressure and compositions.